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EVALUATION OF NAPHTHENE RICH TURBINE FUELS AS HEAT
SINKS FOR HYPERSONIC AIRCRAFT(U) J AND A ASSOCIATES INC
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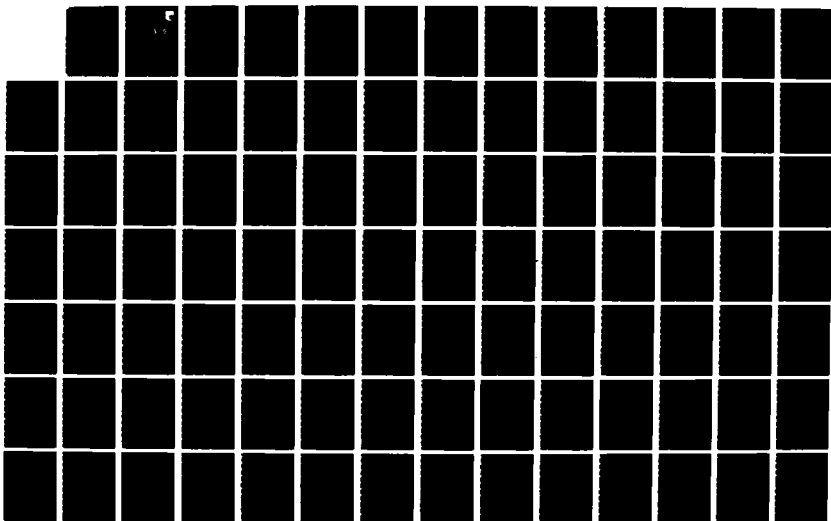
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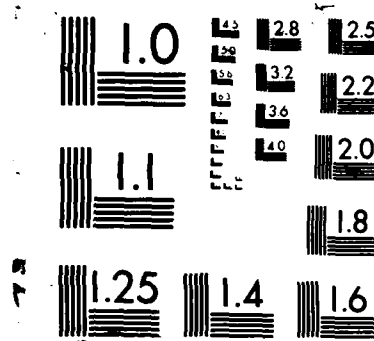
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EVALUATION OF NAPHTHENE RICH TURBINE FUELS AS HEAT SINKS
FOR HYPERSONIC AIRCRAFT



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Final Report for Period July 1986 - December 1986

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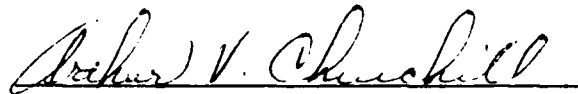
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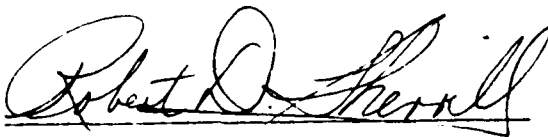


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| <p>A three phase program was undertaken to evaluate the current domestic production of naphthene rich turbine fuels. The first phase was a refinery survey to determine the magnitude of this production and its quality. Hydrocracker effluents are the chief source of these streams, and their turbine fuel out is approximately 500,000 barrels per day. Samples were obtained from 20 domestic refiners and characterized for their naphthene and sulfur contents. Most sulfur contents were low, <2 wppm, and the naphthene contents ranged from 18 to 52 mole percent.</p> <p style="text-align: right;">(Continued on reverse)</p> | | | | | |
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The second phase of the program was to build and shakedown a high liquid space velocity catalytic reformer reactor. Tests were run on pure streams of model naphthenic hydrocarbon compounds using a commercial catalyst similar to that used in previous USAF research. Conversions of the naphthenic compounds to aromatics were high at moderate liquid space velocities, e.g., 100 hr⁻¹. Little cracking of these feeds was observed.

The third phase of the program was to monitor the behavior of some select refinery samples in the high velocity reformer. It was found that 25 atmospheres of hydrogen overpressure was needed to maintain catalyst activity. This hydrogen overpressure was not needed with the pure model compounds. Conversions of the naphthenic portion of the select refinery streams were about 25 percent. This afforded an endotherm of about 100 Btu/lb of whole fuel. It was concluded that in order to obtain a heat sink sufficient for hypersonic aircraft applications two major areas need further development: 1) stream pretreatment to further enrich the naphthene content to 90 mole %; and 2) catalyst activity to achieve greater conversions.



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PREFACE

This report was prepared by J&A Associates, Inc., Golden, Colorado 80401 in fulfillment of United States Air Force Contract No. F33615-86-C-2664. This contract was awarded under the Small Business Innovation Research (SBIR) Program to J&A Associates' proposal response dated January 29, 1986, to solicitation number AF86-183. The report describes the tasks performed during the period July 1, 1986 to December 31, 1986.

The Contracting Officer for this work was Lynn A. Warner and the Project Engineer was Teresa A. Planeaux, both of Air Force Wright Aeronautical Laboratories, Wright Patterson Air Force Base, Ohio.

The author wishes to thank these personnel for their guidance during the course of this project. The author also wishes to thank Alan C. Nixon, Ph.D., Berkeley, California, for his many helpful discussions and suggestions in carrying out this work.

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I. INTRODUCTION

The objectives of this Small Business Innovation Research (SBIR) program were to determine the current domestic supply of naphthene rich hydrocarbons amenable to endothermic turbine fuel applications. Such an application dictates that besides the obvious criterion of being in the turbine fuel boiling range, the fuel be capable of high space velocity catalytic reforming and thus be a particularly clean stream, i.e., very low in catalyst poisons, chiefly sulfur. The questions to which answers were sought in this Phase I technical effort are listed below:

1. What is the current domestic availability of naphthene rich hydrocarbons?
2. What is the quality of this production? In particular what current volume of supply is in the turbine fuel boiling range, 350°F - 550°F, and is it sulfur free?
3. What is the potential of this resource for use in aircraft cooling applications? Are chemically complex petroleum refinery streams amenable to the high specific throughputs needed?
4. What naphthenic fuel components are most easily dehydrogenated? Can the fuels tolerate the high heat fluxes needed?
5. What total conversions can be obtained at high specific throughputs? How does this affect the potential value of the resource or aircraft cooling?

We sought to answer these inquiries with a three (3) phase program. First a survey of the refineries in the United States was undertaken to determine their present operating volumes. The choice of refiners as the chief domestic source of these materials was obvious since they account for over 90% of the hydrocarbon processing volume in this country. Further we focused primarily on refiners operating hydrocrackers, since the product and recycle streams from these units are notably sulfur free and naphthene rich due to the severity of hydrocracker operating conditions. Hydrotreating and hydrorefining are processes which are too mild to give the extremely low levels of sulfur (<2 wppm) needed. Concurrent with this survey was the solicitation of small samples from these refiners to accurately assess in our own research laboratories the quality of this production. This assessment was made on the basis of ASTM distillations, mass spectral analyses, and sulfur content quantification of the samples received. From this broad based survey several samples could be chosen for further testing.

Further testing consisted of high liquid hourly space velocity reforming of these select materials over a commercial catalyst in a laboratory scale reactor and careful analysis of the products thus formed. The laboratory scale reactor was fabricated of Hastelloy C and extensively monitored during operation for thermal events. Liquid space velocities from 100 to 1000 hr^{-1} were achievable. Feed and product analyses were performed by mass spectral techniques which allowed the determination of as many as 10 classes of compounds in these hydrocarbon materials. With this approach we were able to determine the total conversions obtained as well as the specific conversions of different chemical classes. From these extensive and intensive efforts an assessment can be made of the present operating resource, and more importantly of its value to the United States Air Force as a high volume source of quality endothermic fuels.

II. RESULTS OF REFINERY SURVEY

After surveying the chemical and industrial literature for high volume sources of clean turbine fuel boiling range hydrocarbon streams likely to be naphthene rich, it became apparent that refinery hydrocracker products afforded the best opportunity for further investigation. Hydrocracking capacity in the United States is currently about 1.14 million barrels per day(Ref.1). Hydrocracker products are generally low in sulfur (1-10 wppm), olefins (<1 volume percent), and high in naphthenes (25-50 volume percent). As such they present a unique raw resource for potential endothermic fuel development. The low sulfur avoids catalyst poisoning, the low olefin content imparts thermal stability, and the high naphthene content lends the stream to reforming. On these bases it was decided to contact domestic refiners and solicit samples of their hydrocracker products for characterization in the J&A Associates laboratories.

Approximately forty (40) hydrocrackers are currently operating in the United States. Table 1 lists their capacities and locations. Figure 1 illustrates their geographical diversity. Approximately two thirds of the refineries were contacted directly for solicitation of samples. Response to our inquiries was generally favorable although in some cases our requests were quickly passed to corporate marketing personnel who declined to provide any samples from any of that corporation's refineries.

A steady stream of samples was received during the course of this six month project. To facilitate fulfillment of the tasks in this project in a timely manner several hydrocracker samples solicited during 1985 for another Air Force project were used for our analysis. It should be emphasized that hydrocracker feedstocks, operating conditions, and products can be somewhat variable with seasonal demands. Thus although the product slate may change from summer to winter, particularly with respect to boiling range, the general character of the unit effluent should be reasonably constant being predicated on refinery feedstock supply.

TABLE 1

DOMESTIC HYDROCRACKER CAPACITY IN 1986(Ref.1)

| <u>State</u> | <u>Refinery</u> | <u>Crude Capacity</u> | | <u>Hydrocracker Capacity</u> |
|--------------|---------------------------|-----------------------|-------------|------------------------------|
| | | <u>b/cd</u> | <u>b/sd</u> | <u>b/sd</u> |
| Alaska | Texaco Petroleum Kenai | 72,000 | 80,000 | 9,000 ⁽²⁾ |
| California | Atlantic Richfield* | 211,000 | 220,000 | 22,000 ⁽¹⁾ |
| | Carson | | | |
| | Chevron U.S.A. Inc. | 405,000 | NR | 43,000 ⁽¹⁾ |
| | El Segundo | | | |
| | Richmond | 365,000 | NR | 30,000 ⁽²⁾ |
| | | | | 77,500 ⁽¹⁾ |
| | Exxon Co | 109,000 | 114,000 | 28,000 ⁽¹⁾ |
| | Benicia | | | |
| | Golden West Ref. | 40,600 | 42,300 | 11,000 ⁽¹⁾ |
| | Santa Fe Springs | | | |
| | Mobil Oil Corp. | 123,500 | 130,000 | 21,700 ⁽¹⁾ |
| | Torrance | | | |
| | Pacific Refining* | 55,000 | NR | 3,500 ⁽¹⁾ |
| | Hercules | | | |
| | Shell Oil Co.* | 113,500 | 117,000 | 27,000 ⁽¹⁾ |
| | Martinez | | | |
| | Superior Processing | NR | 46,000 | 7,800 ⁽¹⁾ |
| | Santa Fe Springs | | | |
| | Texaco Refining* | 75,000 | 78,400 | 20,000 ⁽¹⁾ |
| | Wilmington | | | |
| | Tosco Corp.* | 126,000 | 132,600 | 20,000 ⁽¹⁾ |
| | Martinez | | | |
| | Unocal Corp. | 108,000 | 111,000 | 22,000 ⁽¹⁾ |
| | Los Angeles | | | |
| | Rodeo | 118,000 | 125,100 | 32,500 ⁽¹⁾ |

TABLE 1
(Continued)

DOMESTIC HYDROCRACKER CAPACITY IN 1986

| <u>State</u> | <u>Refinery</u> | <u>Crude Capacity</u> | | <u>Hydrocracker Capacity</u> |
|--------------|------------------------------------|-----------------------|-------------|------------------------------|
| | | <u>b/cd</u> | <u>b/sd</u> | <u>b/sd</u> |
| Delaware | Texaco Refining* Delaware City | 140,000 | 150,000 | 19,000 ⁽⁴⁾ |
| Hawaii | Hawaiian Indep.* Ewa Beach | 61,500 | 67,900 | 16,000 ⁽¹⁾ |
| Illinois | Clark Oil & Refin.* Blue Island | 64,600 | 68,000 | 11,000 ⁽¹⁾ |
| | Marathon Petroleum* Robinson | 195,000 | 205,000 | 22,000 ⁽¹⁾ |
| | Shell Oil Company Wood River | 264,000 | 276,000 | 33,500 ⁽¹⁾ |
| | Total Petroleum* Arkansas City | 50,000 | 52,200 | 3,190 ⁽¹⁾ |
| Louisiana | Citgo Petroleum* Lake Charles | 320,000 | 330,000 | 35,000 ⁽¹⁾ |
| | Exxon Company Baton Rouge | 455,000 | 474,000 | 24,000 ⁽¹⁾ |
| | Shell Oil Company Norco | 218,000 | 225,000 | 27,700 ⁽¹⁾ |
| | Tenneco Oil Co* Chalmette | 137,000 | 144,000 | 18,000 ⁽¹⁾ |
| | Texaco Refining Convent | 225,000 | 240,000 | 35,000 ⁽²⁾ |
| | Chevron U.S.A. Pascagoula | 295,000 | NR | 68,000 ⁽¹⁾ |

TABLE 1
(Continued)

DOMESTIC HYDROCRACKER CAPACITY IN 1986

| <u>State</u> | <u>Refinery</u> | <u>Crude Capacity</u> | | <u>Hydrocracker Capacity</u> |
|--------------|--|-----------------------|-------------|--|
| | | <u>b/cd</u> | <u>b/sd</u> | <u>b/sd</u> |
| Montana | Exxon Company Billings | 42,000 | 44,000 | 4,900 ⁽¹⁾ |
| Ohio | Standard Oil Co. Lima | 168,000 | 177,000 | 20,000 ⁽⁴⁾ |
| | Toledo* | 120,000 | 126,000 | 35,000 ⁽⁴⁾ |
| | Sun CI-Toledo* | 118,000 | 124,000 | 28,000 ⁽¹⁾ |
| Oklahoma | Kerr-McGee Refining Wynnewood* | 43,000 | 45,000 | 5,000 ⁽¹⁾ |
| Pennsylvania | Atlantic Refining* Philadelphia | 125,000 | 130,000 | 30,000 ⁽⁴⁾ |
| | BP Oil Inc. Marcus Hook | 168,000 | 177,000 | 25,000 ⁽⁴⁾ |
| Texas | Amoco Oil Co. Texas City | 400,000 | 415,000 | 53,000 ⁽¹⁾ 60,000 ⁽²⁾ |
| | Coastal States Pet.* Corpus Christi | 95,000 | NR | 10,000 ⁽¹⁾ |
| | Exxon Co. U.S.A. Baytown | 494,000 | 525,000 | 19,000 ⁽¹⁾ |
| | Mobil Oil Corp.* Beaumont | 270,000 | 285,000 | 32,000 ⁽¹⁾ |
| | Shell Oil Company Deer Park | 228,500 | 240,000 | 65,000 ⁽⁴⁾ |
| | Texaco Refining Port Arthur* | 250,000 | 278,000 | 15,000 ⁽¹⁾ |

TABLE 1
(Continued)

DOMESTIC HYDROCRACKER CAPACITY IN 1986

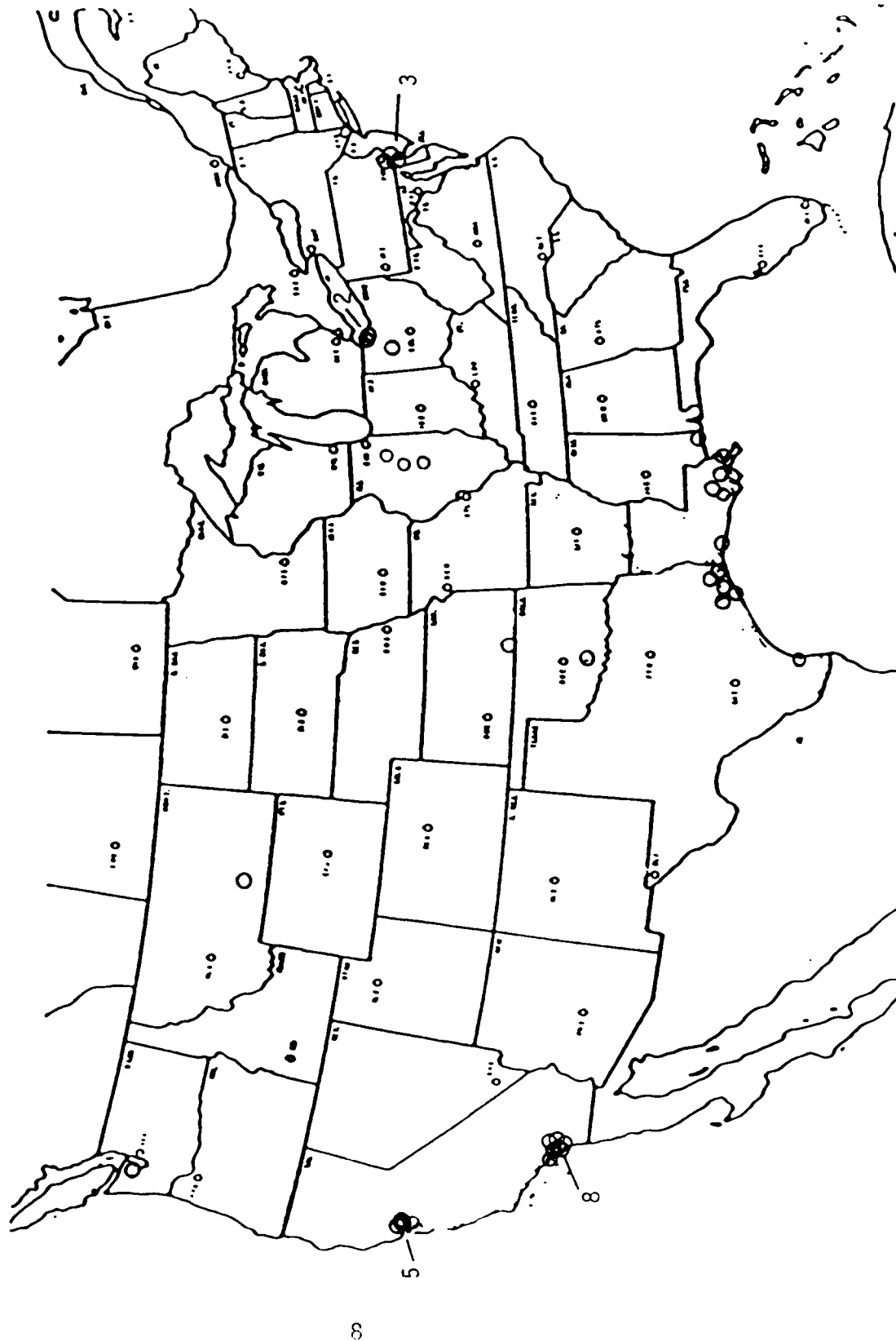
| <u>State</u> | <u>Refinery</u> | <u>Crude Capacity</u> | | <u>Hydrocracker Capacity</u> |
|--------------|---------------------|--------------------------|-------------|------------------------------|
| | | <u>b/cd</u> | <u>b/sd</u> | <u>b/sd</u> |
| Washington | Atlantic Richfield* | | | |
| | Cherry Point | 156,000 | 162,000 | 50,000 ⁽¹⁾ |
| | Total Capacity | 7,070,200 ⁽⁵⁾ | NA | 1,139,290 |

- (1) Distillate upgrading.
 - (2) Residual upgrading.
 - (3) Lube-oil manufacture.
 - (4) Other.
 - (5) Using b/sd for Superior Processing.
- b/cd Barrels per calender day.
b/sd Barrels per shift day.

Refineries which are starred (*) are those from which samples have been received and analyzed.

FIGURE 1
HYDROCRACKER LOCATIONS

ALASKA



HAWAII

Table 2 details the origins of the twenty four (24) samples analyzed in our survey. The refinery location, hydrocracker total capacity, sample stream volume and stream description are given therein. The actual samples obtained from the refiners depend upon the sampling points available at the refinery source. Figure 2 is a generalized flow scheme of a hydrocracker unit. Cycle oil distillation cuts are first treated in a hydrodenitrification (HDN) unit in a pretreatment step. The intermediate stream between the HDN and the hydrocracker (HC) is often monitored for HDN efficiency. Thus some entries in Table 2 are described as intermediate samples. Similarly, kerosene or jet cut materials and recycle streams for further hydrocracking treatment are also monitored and thus available for sampling. It was sought in this project to obtain samples in the 350-500°F boiling range. The actual samples obtained depended upon what sampling points were conveniently available to the cooperating refiner.

The total hydrocracker capacity listed in Table 2 is 421,700 barrels per day or 37% of current domestic capacity. The samples in hand for this project represent 185,800 barrels per day production or 16.3% of the listed total hydrocracker capacity of 1.14 million barrels per day. Since our sampling represents streams totaling 37% of the total domestic capacity, it is reasonable to extrapolate the 185,800 barrels per day to a normalized 502,000 barrels per day of kerosene, recycle and intermediate streams. The difference between this normalized volume and total hydrocracker capacity is most likely to be found in lighter products such as gas and gasoline.

The samples in hand were then characterized for sulfur content and chemical species type. Table 3 gives the results of this characterization. The majority of the samples were very low in sulfur, <2 wppm. Some however were quite sour reaching a sulfur content as high as 2800 wppm (0.28 weight percent). Such a surprisingly high sulfur content could be due to contamination at the point of sampling. API gravities ranged from about 30-50 in accord with the refiners' descriptions of the 30° API sample as #2 fuel oil (Sample 6) and the 50° API sample as kerosene (Sample 7). The naphthene contents of the samples ranged from 18 to 52 mole percent.

TABLE 2
SURVEY PRODUCTION DATA FOR SAMPLES RECEIVED

| <u>Sample</u> | <u>Refinery</u> | <u>H/C Capacity b/sd</u> | <u>Sample Stream b/sd</u> | <u>Stream Description</u> ⁽¹⁾ |
|---------------|---|------------------------------|-------------------------------|--|
| 1 | Atlantic Richfield Carson, California | 22,000 | 1,400 | Kerosene |
| 2 | Pacific Refining Hercules, California | 3,500 | 1,000 | Diesel |
| 3 | Shell Oil Company Martinez, California | 27,000 | 10,000 | Intermediate |
| 4 | Texaco Refining & Marketing, Inc. Wilmington, California | 20,000 | 14,000 | Heavy Crackate |
| 5A&B | Tosco Corporation Martinez, California | 20,000 | A 8,000 B 20,000 | Recycle Intermediate |
| 6 | Texaco Refining & Marketing, Inc. Delaware City, Delaware | 19,000 | 17,000 | #2 Fuel Oil |
| 7 | Hawaiian Independent Refining, Inc. Ewa Beach, Hawaii | 16,000 | 4,800 | Kerosene |
| 8 | Clark Oil and Ref. Corp. Blue Island, Illinois | | 11,000 | 4,000 Recycle |
| 9 A&B | Marathon Petroleum Co. Robinson, Illinois | 22,000 | A 8,000 B 1,000 | Recycle Distillate |
| 10 | Total Petroleum, Inc. Arkansas City, Arkansas | 3,200 | 1,200 | Recycle |
| 11 | Citgo Petroleum Corp. Lake Charles, Louisiana | 35,000 | 7,000 | Kerosene |
| 12 A&B | Tenneco Oil Company Chalmette, Louisiana | 18,000 | A 6,000 B 18,000 | Kerosene Intermediate |

(1) See Figure 2 for explanation.

TABLE 2
(Continued)
SURVEY PRODUCTION DATA FOR SAMPLES RECEIVED

| <u>Sample</u> | <u>Refinery</u> | <u>H/C Capacity b/sd</u> | <u>Sample Stream b/sd</u> | <u>Stream Description</u> ⁽¹⁾ |
|---------------|--|------------------------------|-------------------------------|--|
| 13 | Standard Oil Co. of Ohio Toledo, Ohio | 35,000 | 10,000 | Kerosene |
| 14 | Sun Oil Company Toledo, Ohio | 28,000 | 8,400 | Kerosene |
| 15 | Kerr McGee Refining Corp. Wynnewood, Oklahoma | 5,000 | 1,500 | Distillate |
| 16 | Atlantic Refining & Marketing Corp. Philadelphia, Pennsylvania | 30,000 | 12,000 | Recycle |
| 17 A&B | Coastal States Petroleum Co. Corpus Christi, Texas | 10,000 | A 7,500 B 8,000 | Whole Product Intermediate |
| 18 | Mobil Oil Corp. Beaumont, Texas | 32,000 | 25,000 | Recycle |
| 19 | Texaco Refining & Marketing, Inc. Port Arthur, Texas | 15,000 | 4,000 | Jet Cut |
| 20 | Atlantic Richfield Corp. Cherry Point, Washington | 50,000 | 10,000 | Jet Cut |

(1) See Figure 2 for explanation.

TABLE 3

CHARACTERIZATION OF SURVEY SAMPLES

| Sample Number | API Gravity | Sulfur Content (wppm) | Mole Percents of | | |
|------------------|-------------|--------------------------|------------------|------------|----------|
| | | | Paraffin | Napththene | Aromatic |
| 1 | 37.5 | 3.0 | 35.9 | 27.3 | 36.7 |
| 2 | 37.0 | 2.1 | 49.1 | 28.0 | 22.9 |
| 3 | 34.6 | <2 | 15.1 | 40.2 | 44.7 |
| 4 | 48.9 | <2 | 26.6 | 51.8 | 21.6 |
| 5A | 38.0 | <2 | 24.6 | 44.7 | 30.7 |
| 5B | 33.5 | <2 | 10.0 | 53.0 | 37.0 |
| 6 | 29.7 | 20 | 15.7 | 43.7 | 40.6 |
| 7 | 49.0 | <2 | 50.6 | 42.1 | 7.3 |
| 8 | 38.6 | 19.3 | 32.2 | 55.6 | 12.2 |
| 9A | 49.8 | <2 | 63.3 | 18.4 | 18.3 |
| 9B | 40.4 | <2 | 22.6 | 47.4 | 30.0 |
| 10 | 40.8 | <2 | 60.4 | 17.9 | 21.7 |
| 11 | 39.2 | <2 | 23.2 | 43.9 | 32.9 |
| 12A | 42.5 | <2 | 39.1 | 46.4 | 14.5 |
| 12 | 32.1 | 141 | 42.2 (1) | 41.2 (1) | 16.6 (1) |
| 13 | 43.4 | <2 | 37.5 | 45.7 | 16.0 |
| 14 | 46.7 | <2 | 67.5 | 18.1 | 14.4 |
| 15 | 41.9 | 633 | 39.2 | 47.9 | 12.9 |
| 16 | 43.3 | 13.8 | 49.7 (1) | 33.6 (1) | 16.7 (1) |
| 17A | 44.9 | 55.7 | 38.9 (1) | 34.1 (1) | 27.0 (1) |
| 17B | 30.8 | 2800 | 21.6 (1) | 50.5 (1) | 27.9 (1) |
| 18 | 37.0 | 6.1 | 37.3 | 44.3 | 17.4 |
| 19 | 39.1 | <2 | 23.3 | 35.6 | 41.1 |
| 20 | 41.0 | <2 | 30.4 | 36.5 | 33.1 |

(1) Performed on the kerosene fraction of the whole sample because the latter contained much heavy material which could not be analyzed in the mass spectrometer.

All samples were further characterized by ASTM D-86 distillation. These data are given in Table 4. Samples 4 and 9A were quite light, having distillation end points lower than the turbine fuel initial boiling point (IBP). This is despite their being described as heavy crackate and recycle streams respectively. Several other samples (9B, 10, 12B, 17A, 17B) extended into the heavy cycle oil boiling range.

From these characterizations an estimate of the volume of turbine fuel naphthenes can be made. Table 5 lists the estimated volume of naphthene hydrocarbons occurring in these clean turbine boiling range cuts. The average volume in this boiling range being 65%, and the average naphthene content of the whole stream being 26%, the estimated naphthene jet fuel volume is 60,000 barrels per day for the capacity represented here. This can be normalized to an estimated 162,000 barrels per day nationwide. The current Air Force consumption of jet fuel being 300,000 barrels per day, this naphthene volume may appear small, but it must be remembered that this endothermic fuel will be needed in much lower volume than total Air Force demands because of the special mission applications of this fuel.

TABLE 4

ASTM D-86 DISTILLATIONS OF HYDROCRACKER SAMPLES

| Sample Number | Corrected(1) Temperature (°F) Observed at Overhead Volumes Percents of | | | | | | | | | | | | |
|------------------|--|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|--------|
| | IBP | 5 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 | EP |
| 1 | 268 | 352 | 367 | 381 | 394 | 407 | 420 | 432 | 443 | 457 | 483 | 501 | 507 |
| 2 | 295 | 433 | 462 | 507 | 538 | 560 | 580 | 595 | 606 | 614 | 620 | 629 | 630 |
| 3 | 270 | 368 | 382 | 394 | 404 | 412 | 420 | 428 | 436 | 446 | 460 | 482 | 486 |
| 4 | 201 | 239 | 251 | 262 | 270 | 279 | 286 | 297 | 309 | 326 | 348 | 360 | 362 |
| 5A | 318 | 403 | 411 | 420 | 426 | 432 | 439 | 446 | 460 | 483 | 516 | 541 | 549 |
| 5B | 262 | 289 | 363 | 414 | 437 | 452 | 467 | 483 | 503 | 529 | 554 | 578 | 578 |
| 6 | 269 | 395 | 425 | 453 | 475 | 491 | 505 | 523 | 542 | 564 | 599 | 633 | 646 |
| 7 | 236 | 296 | 305 | 326 | 346 | 359 | 378 | 397 | 424 | 456 | 494 | 505 | 506 |
| 8 | 283 | 385 | 409 | 437 | 458 | 475 | 491 | 505 | 518 | 542 | 580 | 601 | 601 |
| 9A | 246 | 248 | 250 | 254 | 261 | 268 | 278 | 289 | 302 | 319 | 343 | 351 | 356 |
| 9B | 395 | 442 | 452 | 469 | 481 | 494 | 511 | 540 | 590 | 652 | 703 | 707 | 707 |
| 10 | 338 | 414 | 448 | 484 | 512 | 548 | 603 | 628 | 658 | 682 | 708 | 711 | 711 |
| 11 | 148 | 296 | 344 | 378 | 396 | 411 | 428 | 445 | 460 | 490 | 520 | 531 | 531 |
| 12A | 290 | 368 | 380 | 391 | 401 | 410 | 419 | 427 | 434 | 443 | 454 | 462 | 467 |
| 12B | 124 | 440 | 503 | 572 | 601 | 629 | 664 | 690 | 708 | 724 | -- | -- | 724(80 |
| 13 | 189 | 341 | 366 | 387 | 400 | 413 | 422 | 431 | 439 | 451 | 464 | 467 | 467 |
| 14 | 319 | 418 | 432 | 446 | 455 | 465 | 474 | 483 | 493 | 504 | 521 | 530 | 532 |
| 15 | 271 | 406 | 419 | 430 | 439 | 446 | 454 | 460 | 470 | 481 | 493 | 501 | 504 |
| 16 | 317 | 389 | 405 | 435 | 459 | 482 | 508 | 530 | 557 | 587 | 619 | 632 | 632 |
| 17A | 134 | 212 | 231 | 280 | 327 | 375 | 453 | 558 | 630 | 679 | -- | -- | 703(80 |
| 17B | 135 | 504 | 556 | 607 | 653 | 680 | 705 | 730 | -- | -- | -- | -- | 730(60 |
| 18 | 273 | 333 | 357 | 414 | 477 | 527 | 560 | 589 | 614 | 641 | 678 | 684 | 684 |
| 19 | 260 | 349 | 361 | 375 | 387 | 399 | 413 | 430 | 447 | 469 | 494 | 510 | 510 |
| 20 | 313 | 379 | 386 | 396 | 404 | 410 | 418 | 427 | 440 | 458 | 481 | 494 | 501 |

(1) Distillation temperatures corrected to 760 mm Hg atmospheric pressure.

TABLE 5

| Sample | Vol % In | Mole % | Volume % | Stream | Volume |
|---------------|----------------------|------------------|------------------|---------------|------------------|
| <u>Number</u> | <u>350°F - 550°F</u> | <u>Naphthene</u> | <u>Naphthene</u> | <u>Volume</u> | <u>Naphthene</u> |
| | | | | <u>(b/sd)</u> | <u>(b/sd)</u> |
| 1 | 95.1 | 27.3 | 26.0 | 1400 | 364 |
| 2 | 33.5 | 28.0 | 9.4 | 1000 | 94 |
| 3 | 95.9 | 40.2 | 38.6 | 10000 | 3860 |
| 4 | 9.2 | 51.8 | 4.8 | 14000 | 6720 |
| 5A | 98.1 | 44.7 | 43.9 | 8000 | 3512 |
| 5B | 79.3 | 53.0 | 42.0 | 20000 | 8400 |
| 6 | 70.4 | 43.7 | 30.8 | 17000 | 5236 |
| 7 | 66.9 | 42.1 | 28.2 | 4800 | 1354 |
| 8 | 78.8 | 55.6 | 43.8 | 11000 | 4818 |
| 9A | 5.6 | 18.4 | 1.0 | 8000 | 80 |
| 9B | 62.0 | 47.4 | 29.4 | 1000 | 294 |
| 10 | 39.6 | 17.9 | 7.1 | 1200 | 85 |
| 11 | 88.2 | 43.9 | 38.7 | 7000 | 2709 |
| 12A | 96.2 | 46.4 | 44.6 | 6000 | 2676 |
| 12B | 13.2 | 41.2 | 5.4 | 18000 | 972 |
| 13 | 93.2 | 45.7 | 42.6 | 10000 | 4260 |
| 14 | 98.4 | 18.1 | 17.8 | 8400 | 1487 |
| 15 | 97.1 | 47.9 | 46.5 | 1500 | 698 |
| 16 | 65.1 | 33.6 | 21.9 | 12000 | 2628 |
| 17A | 24.5 | 34.1 | 8.4 | 7500 | 630 |
| 17B | 6.5 | 50.5 | 3.3 | 8000 | 264 |
| 18 | 38.4 | 44.3 | 17.0 | 25000 | 4250 |
| 19 | 94.6 | 35.6 | 33.7 | 4000 | 1348 |
| 20 | 97.2 | 36.5 | 35.5 | 10000 | 3550 |

III. REFORMER UNIT FIX UP AND EXPERIMENTAL PROCEDURES

1. Feedstocks Used

- a. Pure Compounds: These feeds were used to confirm earlier work(2) and to verify the workability of the pilot plant configuration. They consisted of methylcyclohexane from Phillips 66, Bartlesville, Oklahoma (99 mole % pure, Lot H084, UN 2296) and decahydronaphthalene from DuPont, Wilmington, Delaware (Technical Decalin solvent, 50/50 cis/trans, Lot 272, Code 192400, UN 1147).
- b. Hydrocracker Samples: These feedstocks were chosen from the survey conducted earlier (see Section II above) on the basis of hydrocarbon composition, boiling range, and sulfur content. These feeds, obtained in drum lots, were as follows:
 - (1) Tosco Corporation, Avon, CA refinery, hydrocracker diesel, 38.00 API gravity.
 - (2) CITGO, Lake Charles, LA refinery, hydrocracker kerosene, 40.80 API gravity.
 - (3) ARCO, Carson, CA refinery, hydrocracker distillate, 37.50 API gravity. (This sample was obtained in place of a sample originally requested from the ARCO, Cherry Point, WA refinery). Due to a change in the program, this feed was not tested.

(4) An equal part composite of 11 hydrocracker samples obtained from a survey conducted in 1985, 39.9° API gravity. This sample was prepared in case one of the above feeds failed to arrive in time for testing. This feedstock also was not tested due to a change in the program.

c. Hydrogen: Hydrogen used for catalyst reduction, reactor pressurization, and supplemental input during runs, was obtained in standard gas cylinders, at 99.9% purity, from General Air, Denver, CO.

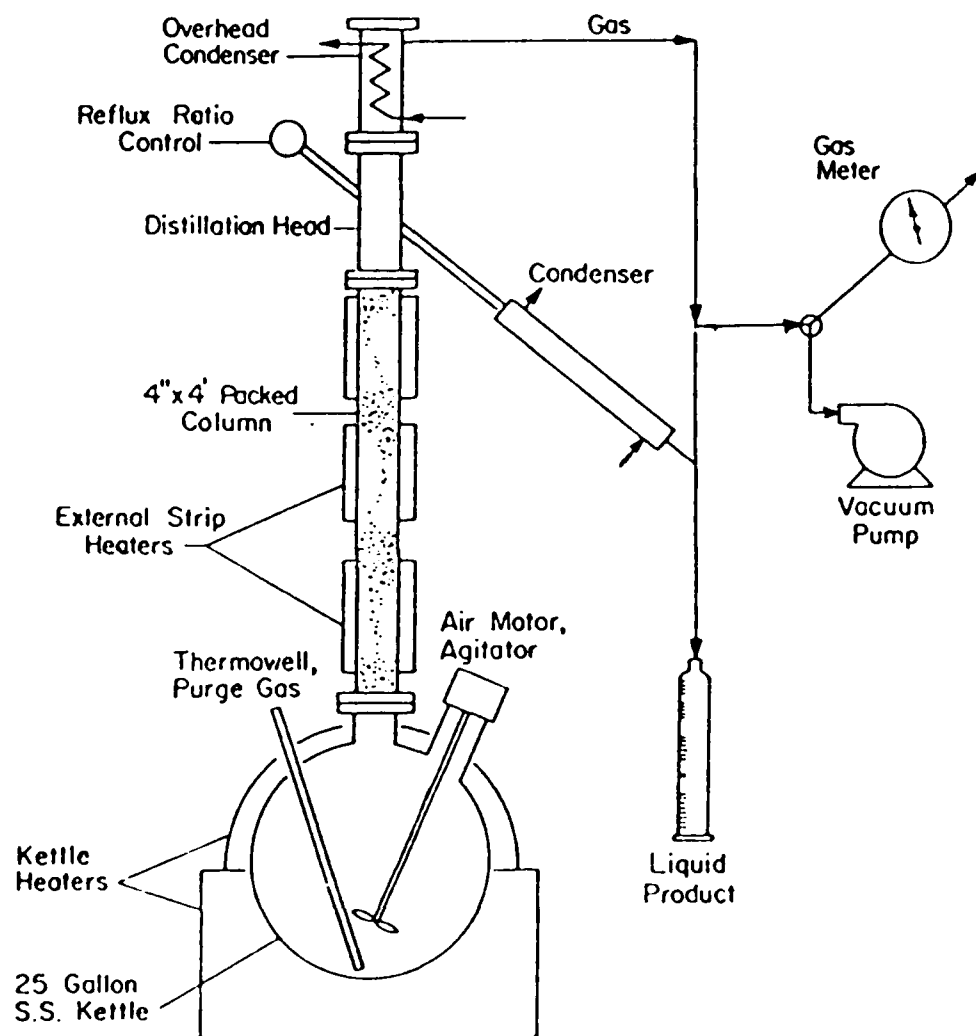
2. Feedstock Preparation

a. Pure Compounds: The methylcyclohexane was used as received with no further processing. Sulfur content was less than 2 wppm. The drum of decahydronaphthalene was distilled in order to maximize the concentration of the trans isomer. The apparatus used was the 25 gallon batch still illustrated in Figure 3. The procedure used closely followed ASTM D 2892 (True Boiling Point (TBP), or 15/5 distillation) except that the reflux ratio was increased to 30:1 (3% take-off) in order to improve the cis-trans separation. The maximum separation achieved was 95% trans, and this was blended back to 91% T in order to duplicate the feed used in earlier work(Ref.3).

b. Hydrocracker Samples: These samples were distilled by the 25 gallon batch still, following the ASTM D 2892 procedure, in order to obtain the following fractions: IBP-350°F, 350-420°F, 420-450°F, and 450°F+. The first cut, if present, was rejected, and the latter fractions were used as

FIGURE 3

25 GALLON BATCH STILL



individual feedstocks, along with the whole, undistilled hydrocracker sample. Thus 1 sample provided 4 feedstocks. Only the Tosco and CITGO samples were distilled; the program tasks were altered after the above feeds had been run and it became unnecessary to distill either the ARCO or the composite sample. Distillation results on the Tosco and CITGO sample are given in Appendix D.

- c. Additional Sample Preparation: Due to very low conversions on the early hydrocracker fraction tests, one feedstock (Tosco 350-420°F) was clay treated prior to testing. The feed was percolated through a 5' column of 30-60 mesh Attapulgate (obtained from Engelhard Minerals and Chemicals Division, Attapulcus, GA.) in order to reduce the concentration of polar compounds and to lower the nitrogen content.

All feedstocks were transferred to an 8 gallon capacity feed bomb where nitrogen gas was bubbled through the feed for 1.5-2.0 hrs in order to displace any dissolved oxygen. The feed was then maintained under approximately 5 psig nitrogen pressure, while in the bomb.

3. Catalysts Used

For all tests except one, the reforming catalyst used was R-8 reference catalyst, obtained from UOP, Process Division, Riverside, Illinois. This catalyst was chosen because it had been used in earlier work(Ref2) and could provide a bridge to those earlier results. UOP R-8 consists of 1/16 inch alumina spheres, containing approximately 1% platinum, and having a bulk density of approximately 0.52 g/cc. No analysis of this catalyst was made nor allowed by J&A Associates' agreement with UOP, Inc.

One test used Englehard E 302 reforming catalyst. This catalyst consists of 1/16" extrudate having a bulk density of approximately 0.65 g/cc. No analyses were performed on this catalyst either.

Catalysts were diluted in most runs with inert materials in order to enhance heat transfer to the catalyst particles. Initial runs used copper shot as a diluent (#CX1935-1 obtained from EM Science, Cherry Hills, N.J.) because earlier work(Ref2) had used this approach. However, due to problems with the copper shot (agglomeration under heat, discoloration and possible effect on the reaction, and segregation due to the high bulk density of 4.9 g/cc) alumina beads were used as diluent in most tests. These beads were 1/16" alumina grinding media, obtained from Coors, Golden, CO having a bulk density of 2.1 g/cc.

4. Catalyst Preparation

Catalysts required reduction before a run in order to alter the platinum salts to the active elemental state. This reduction or activation was carried out in-situ for each catalyst charge immediately prior to, or a day prior to, the actual test. This minimized any degradation (moisture adsorption, oxidation) of catalysts that may have resulted from a single-batch reduction process. The in-situ reduction consisted of the following steps:

- a. Catalysts and diluent were measured out by volume and mixed together. (Virgin UOP R-8 catalyst was bright white, virgin Engelhard E302 was a "dirty" white color). Due to high static charges on the catalyst, the mixing was performed in a metal beaker.

- b. The charge was loaded into the reactor in small scoops. Each scoopful was adjusted to have the approximate desired concentration of catalyst in order to minimize segregation in the reactor. The catalyst bed was contained by small plugs of stainless steel mesh.
- c. The loaded reactor was plumbed into the reformer pilot plant system, a nitrogen purge was attached, and the reactor heaters were turned on.
- d. The reactor was heated to 400°F over a 1.5 hour period with a constant nitrogen sweep. This thoroughly dried the catalyst and displaced any air in the system.
- e. Temperatures were then gradually increased to 1100°F over a 1-2 hour period, replacing the nitrogen sweep with a hydrogen input of approximately 5 SCFH. Also, unit pressure was brought up to target operating pressures, using hydrogen.
- f. The target pressures, hydrogen sweep, and 1100°F temperature were maintained for 1 hour. Then the heats were turned off and the system was either blocked in under pressure (when making a run on the following day), or the system was allowed to cool to the target temperature, at which point the run was started (same day running). In both cases, between reduction and run initiation, the catalyst was maintained under a hydrogen atmosphere.

Catalyst reduced in the above manner showed a uniform, light gray color. Catalyst that had been heated under an air atmosphere, by contrast, showed a non-uniform distribution of white, gray, and blue colored particles.

The above procedure was settled on after less severe treatment resulted in rapid catalyst deactivation. However, the above procedure may not be optimum and should be investigated further.

5. Test Apparatus

The reformer pilot plant used for these tests consisted of a modified hydrotreating/isocracking unit, originally designed and built in 1964, at the Tidewater Refinery, Avon, California with the assistance of the California Research Corporation, Richmond, California. The unit was designed for distillate feeds, using pressures up to 3500 psig and temperatures up to 850°F.

In 1981, this unit, along with other pilot plants and sample prep distillation units, was moved to the present J&A Associates site (at that time, the Tosco Corporation Rocky Flats Research Center) where it was upgraded and used for hydrotreater and hydrocracker catalyst evaluation, and for hydrotreating studies on various cat cracker feedstocks (vacuum gas oils). It was also used to hydrotreat potential high density jet fuel candidates for a Wright Patterson Aero Propulsion Laboratory study (Battelle-Columbus Subcontract #G-9046(8827)-544) conducted in 1985. The upgraded hydrotreater system is schematically shown in Figure 4.

As shown in Figure 5, this pilot plant was modified into a high space velocity reformer by the following alterations:

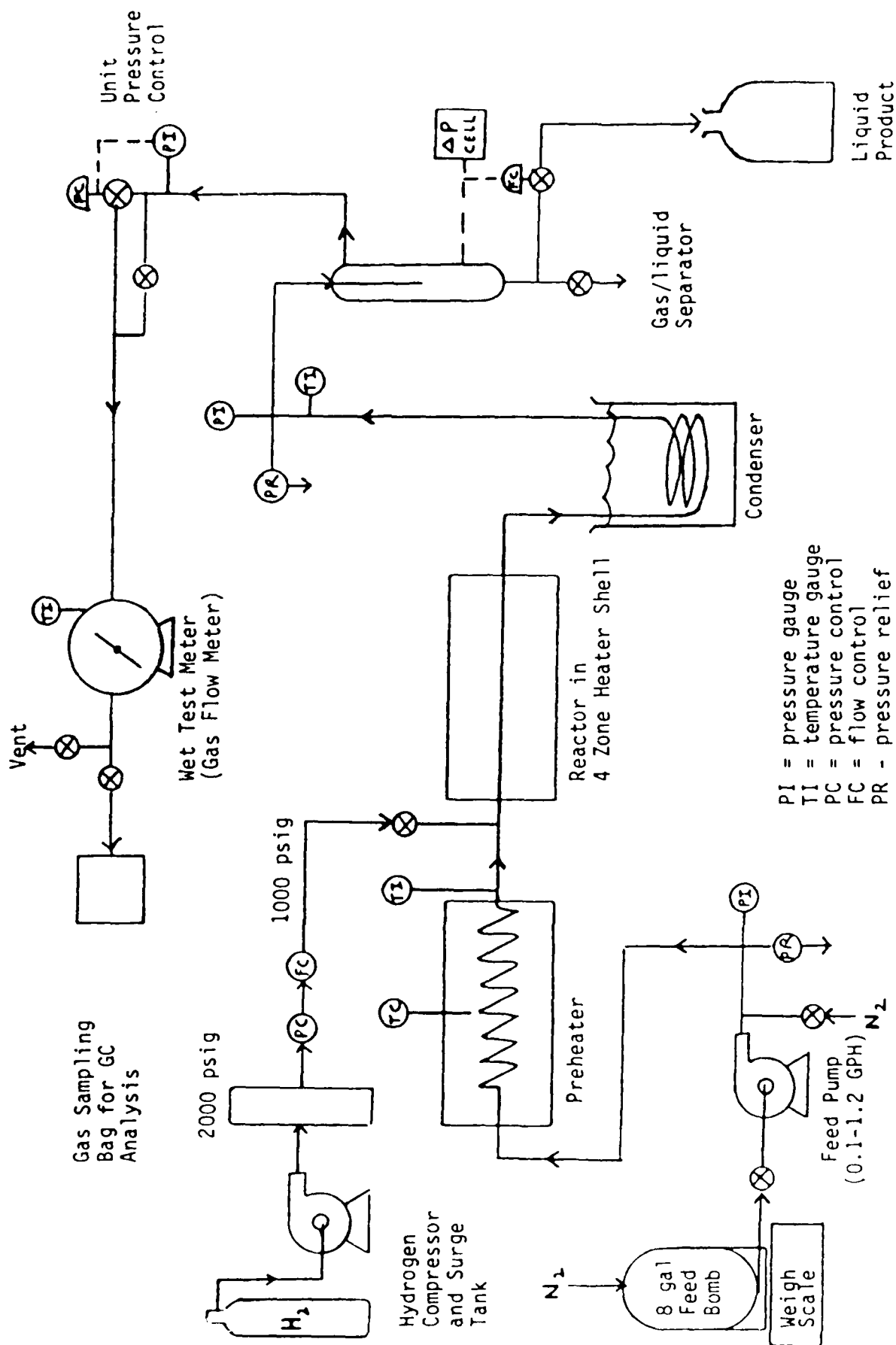
- a. A larger capacity feed pump was installed to handle up to five gallons per hour input.
- b. Feed input was metered by placing an eight gallon capacity feed bomb on a weigh scale, rather than by measuring volume draw-down from 2-1 gallon capacity feed tanks.

FIGURE 4



100

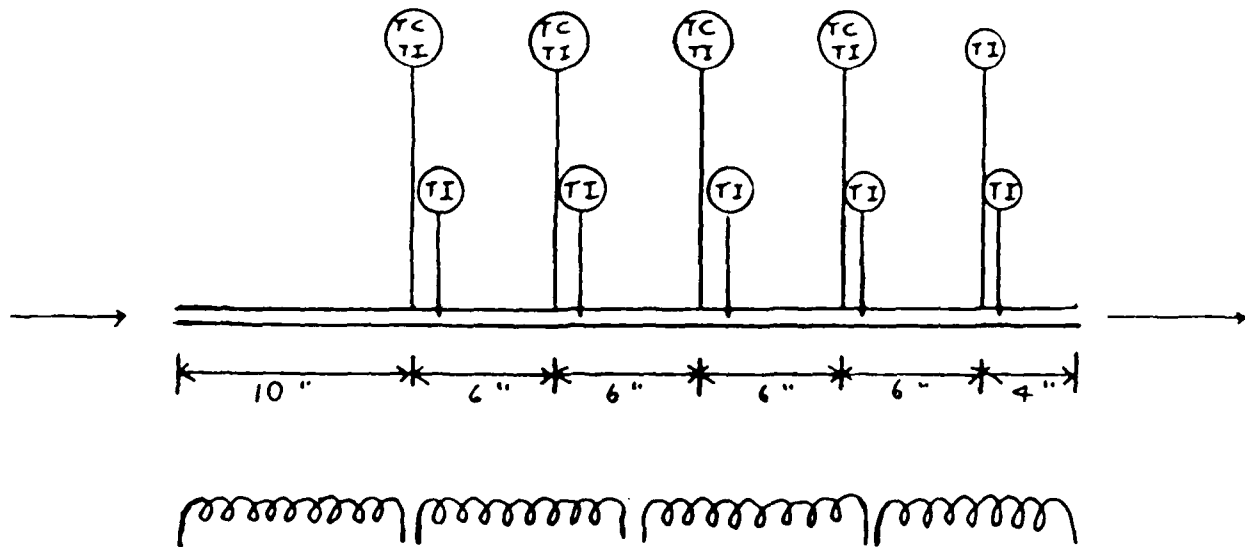
FIGURE 5
REFORMER PILOT PLANT, SBIR CONTRACT F33615-86-C-2664



- c. A 7300 watt preheater was plumbed into the system (Lindbergh Model 54851 tube furnace).
- d. New feed and product lines of 1/4" 304 stainless steel tubing were installed (original lines were thick-walled autoclave tubing).
- e. A new reactor with 10 thermowells was fabricated from 3/8" Hastelloy tubing (Figure 6).
- f. A new reactor heater was fabricated, utilizing four 1750 watt heating zones (7000 watt total).
- g. A water cooled product condensing system was fabricated. (This condenser was bypassed for tests using decahydronaphthalene, which required extensive heat tracing).
- h. A 1 gallon capacity gas/liquid separator was installed in order to break up foam and minimize oil entrainment, and to act like a surge tank for the systems.
- i. Liquid level and back pressure control valves were recalibrated and sized for the anticipated throughput.
- j. Provisions for a debutanizer tower were made in that the product oil line was plumbed into the 25 gallon batch still kettle. This configuration was never used because the conversions and resulting yields of light hydrocarbons were not up to expectations.

FIGURE 5

REFORMER REACTOR, SBIR CONTRACT F33615-86-C-2664



Zone A
1750 W

Zone B
1750 W

Zone C
1750 W

Zone D
1750 W

3/8" x 38" Hastelloy Tubing Reactor

Testing Conditions: Temp \approx 1200°F

Press \approx 25 Atmos

LHSV = 100 - 1000

Catalyst Bed = 3-20 cc

TC = Temperature control

TI = Temperature Read-out

k. The hydrogen input system was altered so that hydrogen did not enter the lines until after the preheat section. This was done to maximize the liquid residence time in the preheater and to prevent slugging in the preheater.

6. Test Procedures

As described earlier, feeds were prepped and loaded into feed bombs. Usually 2 feed bombs were hooked up to the feed pump so that a back-up or alternate feed source was available. Also as described earlier, catalyst was loaded and reduced in-situ before each run. The nominal volume of the catalyst bed was 20 cc, with a 10 cc section at the inlet which was normally filled with inert material (copper shot or alumina beads). This served as a small preheat section and mixing chamber for feed oil and hydrogen (for material balances MB 37 and MB 38, an additional 10 cc section was added to the inlet to serve as a guard bed). For most tests, the 20 cc catalyst bed was diluted 50% with inerts, usually alumina beads.

After catalyst reduction, the reactor was brought to the desired temperature, pressure, and hydrogen input rate (if desired) for the test. Only hydrogen was used to pressurize the system, so that each test was begun in a hydrogen atmosphere. The hydrogen input rate was set under these actual run conditions, without oil being fed, and no further adjustment to hydrogen input was made during the run. In order to ensure a steady hydrogen feed rate, the gas was metered from a controlled 1000 psig source, provided by a hydrogen compressor system originally used for hydrotreating tests. Before this system was implemented, several tests were performed using only hydrogen cylinders, and the input rate was found to drop steadily as the hydrogen cylinder pressure decreased.

Tests with methylcyclohexane, decahydronaphthalene, and early tests on hydrocracker samples did not use hydrogen input. These tests were also conducted at lower pressures (10 atmosphere) than the later tests (25 atmospheres). Since the main intent of the first tests was to confirm earlier work, these tests were not repeated under the more severe conditions required for the hydrocracker samples.

Once the temperature, pressure, and hydrogen input were stabilized at the target conditions, the feed oil was started. Preheater and reactor temperatures dropped significantly upon feed input and required about 1/2 hour to recover. During this 1/2 hour, several weight readings were taken on the feed tank in order to adjust the feed rate. The first runs allowed a 1 hour line-out period, but this was shortened to 1/2 hour for most runs when it was found the catalyst deactivated steadily over time.

After the line-out period, a material balance period was started. This involved zeroing the product gas meter, switching product oil receivers, weighing the feed tank, and starting a timer. Initially, material balance runs were planned to be two (2) hours long, but the relatively rapid catalyst deactivation made one (1) hour runs more realistic for hydrocracker samples.

During the material balance period, data were recorded every half hour for temperatures (13 points), pressure (4 points) and feed rates. Product gas readings were taken either at 1/2 hour or 15 minute intervals and product gas was slowly drawn into an evacuated gas bag over the length of the run. In addition, strip charts recorded all temperatures as well as pressure at the control valve.

At the end of the first material balance (usually conducted at an 840°F skin temperature) the product oil receivers were again switched, the pertinent data recorded, and the temperature control point changed for the second run, usually conducted at 1020°F skin temperature. This normally required a 1/2 hour line-out period, after which another material balance of 1 or 2 hours was made. In most cases, one catalyst charge was used for two (2) consecutive runs, with the lower temperature run being performed first.

The two (2) earliest tests experimented with internal (catalyst bed) temperature control. However, due to the endothermic reaction, so much heat input was requested by the controllers that skin temperatures went higher than desired, causing product cracking and coking. Thereafter, temperature control was by skin thermocouples, as had been the practice in earlier work(1).

At the end of the second balance period, the heats were shut off, the product receivers were switched, the hydrogen input was shut off, but the feed was kept on for an hour in order to cool the system. Shutting off the feed at a 1020°F reactor temperature would probably have resulted in coking, polymerization, and thermal cracking of the oil left in the reactor. The system was slowly depressurized during this cool down. Rapid depressurization could cause catalyst fracture, carryover of solid material to the control valve, and more important, an immediate heat increase due to the depressurization of hydrogen. This latter effect was noted in some of the early runs when problems caused rapid loss of pressure in the system. Temperatures in the catalyst bed increased several hundred degrees Fahrenheit, possibly destroying the catalyst structure or catalytic activity.

After this cool-down, the feed was halted and the system blown down with nitrogen. At this point, the catalyst bed was still at 600-800°F so practically any oil left on the catalyst should have been evaporated or carried away by the subsequent nitrogen sweep. After approximately one (1) hour of nitrogen purge, the reactor was blocked in and allowed to cool completely overnight.

On the following day, the reactor was removed from the system and the spent catalyst removed from the reactor. The color of the spent catalyst was black in all cases. This spent catalyst was bottled and submitted for a coke determination.

Meanwhile, product oil from the material balances had been weighed and was submitted for API gravity determination and hydrocarbon type analysis (PNA). Gas samples collected during the balance period were submitted for normal gas chromatography analysis and, if necessary, for trace hydrocarbon analysis. The latter analysis was requested for runs using hydrogen input, since this input greatly diluted the actual product gas components.

7. Analyses Performed

- a. Feedstock: Feeds were analyzed for API gravity by ASTM D4025 (Digital Density Meter, Mettler/Paar DMA45), for sulfur content by ASTM D 2622 (X-Ray Fluorescence, Siemens SRS 200 spectrometer), and for hydrocarbon types by mass spectrometry (either direct inlet mass spec on a Finnigan MAT 212 or GC/MS on a Carlo Erba 2900 Fractovap GC/Finnigan 3300 M.S.). Some feeds were also analyzed for total nitrogen content by Antek chemiluminescence.

- b. Product Oil: Product oils were analyzed for API gravity and hydrocarbon types, as described above. Sulfur determinations were not made.
- c. Product Coke: Coke on catalyst was determined by catalyst weight loss in an air-swept muffle furnace at 700°C. Prior to this determination, the catalyst was solvent extracted by Soxhlet to remove any adsorbed oil, and oven dried at 200°C to remove solvent and moisture. Corrections were not made for the possible formation of platinum oxides from elemental platinum, since the uniform gray appearance of the de-coked catalyst appeared identical to that of the reduced catalyst.
- d. Product Gas: Product gas was routinely analyzed by gas chromatography using a Hewlett-Packard 5840A GC with the "refinery gas analysis" package (3 sets of column). For runs using hydrogen input, which greatly diluted the product gas components, trace hydrocarbon analyses were also performed, using a Hewlett-Packard 7620A GC and a flame-ionization detector (FID).

IV. MODEL COMPOUND REFORMING RESULTS

To demonstrate the appropriateness of the experimental technique, a series of high space velocity reforming runs were carried out with model compounds over a commercial catalyst. Both the model compounds and the catalyst were similar to ones used in previous USAF/Shell Research. Table 6 lists the conditions and results for these runs. The model compounds were methylcyclohexane (MCH) and decalin (DHN). The latter was enriched in the trans form to 91 weight percent by distillation. Both materials were sulfur free, less than 2 wppm, as determined by X-Ray Fluorescence (XRF).

TABLE 6

REFORMING OF MODEL COMPOUNDS

| <u>MB</u> <u>Number</u> | <u>Feed</u> | <u>Temperature</u> <u>°F</u> | <u>Liquid Hourly</u> <u>Space Velocity</u> | <u>Pressure</u> <u>(psia)</u> | <u>Conversion</u> <u>(mole %)</u> | <u>Previous Conversion</u> <u>(mole %)</u> (Ref. 3) |
|----------------------------|-------------|---------------------------------|---|----------------------------------|--------------------------------------|--|
| 03 | MCH | 840 | 96 | 125 | 63 | 41 |
| 04 | MCH | 1020 | 97 | 110 | 84 | 67 |
| 11 | MCH | 840 | 968 | 150 | 17 | 63 |
| 12 | MCH | 1020 | 994 | 150 | 30 | 84 |
| 07 | DHN | 840 | 88 | 150 | 45 | 50 |
| 08 | DHN | 1020 | 92 | 150 | 58 | 82 |
| 09 | DHN | 840 | 990 | 150 | 2 | 32 |
| 10 | DHN | 1020 | 1010 | 145 | 4 | 59 |

MB = Material Balance

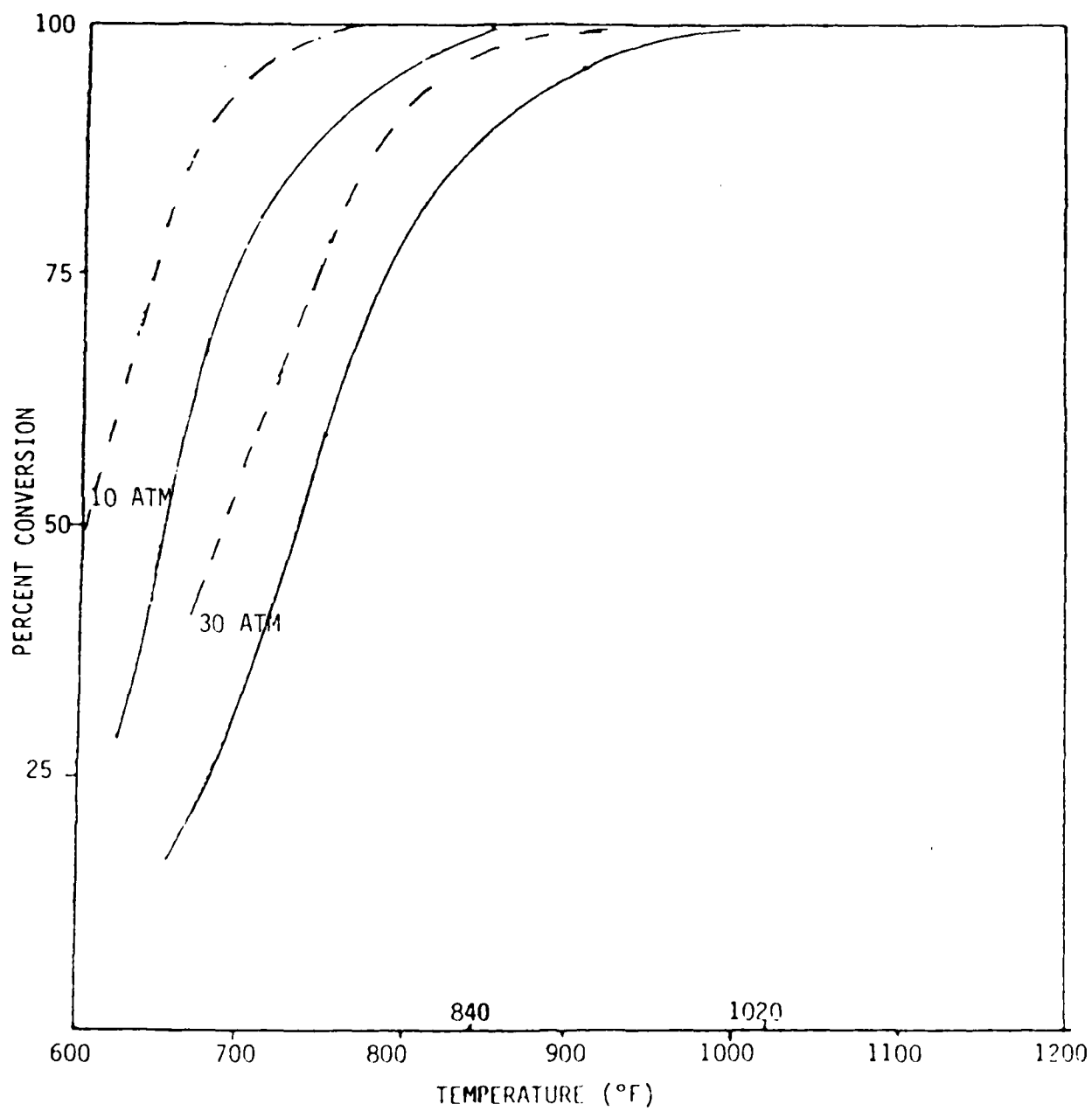
MCH = Methylcyclohexane

DHN = Decalin, 91% trans/9% cis

The results of our new runs are compared to results of runs in the previous work for comparison. The agreement is reasonably good between the two sets of data showing that our packed bed reactor is of an efficiency similar to that of the early USAF/Shell design. We are able to achieve conversions of methylcyclohexane as high as 84% with 99% selectivity for toluene and conversions of decalin as high as 58% with 95% selectivity for naphthalene. Decalin reforming gave lower selectivity because of the partial dehydrogenation of decalin to tetralin. For MB07 this selectivity was only 80%, i.e., 20% of the conversion of decalin was to the partially dehydrogenated species tetralin. The 100 LHSV runs were much more effective than the 1000 LHSV runs. Indeed at 1000 LHSV very little conversion of decalin was effected. The 1020°F runs produced substantially more cracking than the 840°F runs.

It should be noted that the choice of 150 psia pressure was made to provide some back pressure control of pump pulsations as well as serving as a bridge to earlier work. At this pressure neither of the two chemical systems are equilibrium limited as Figure 7 illustrates. Thus, the reactor could be operated at higher pressures, e.g., 375 psia, and still provide effective conversions at the lower space velocities. As will be discussed later, such a situation arose due to catalyst sensitivity.

FIGURE 7
EQUILIBRIUM CONVERSIONS OF METHYLCYCLOHEXANE
(—) AND DECALIN (---) AT 10 AND 30 ATM



V. REFINERY SAMPLE REFORMING RESULTS

Initial Tests.

Following the shakedown and efficiency demonstration of the high space velocity catalytic reformer, tests were begun on the refinery streams chosen on the basis of their high naphthene content, low sulfur content, and geographic diversity. The samples chosen were from central California, Tosco Corp.refinery (sample 5A), Louisiana, CITGO Petroleum Corp. (sample 11), and Washington state, ARCO (sample 20). The latter sample did not arrive in time for testing and thus contract modifications were made. The first two samples were obtained in two drum quantities and distilled to give three cuts: 1) 350-420°F; 2)420-450°F; 3)450+°F. These cuts and a portion of whole fuel were run in this series of tests.

It was found that although the cuts were rich in naphthenic hydrocarbon no reforming activity was taking place. The first set runs were at liquid hourly space velocities of 300 and 100. None of these runs (MB13, MB14, MB15, MB16) gave any naphthene to aromatic conversion. Table 7 lists the mass spectral analyses for the latter two material balance products. Comparison of feed to product compound types shows little change before and after the run. There is a slight increase in product paraffin content with a nearly equal decrease in alkyl benzene content. It might be inferred from this that cracking of alkyl side chains and possible aromatic condensation was leading to the production of coke which deactivates the catalyst. The amount of coke on catalyst for these runs was about 0.88 weight percent, substantially more than that seen for the model compound runs.

It was thought that perhaps trace nitrogen compounds or oxygen gas was causing catalyst deactivation. The procedure for sparging the liquid fuel was thus made more rigorous and the feed treated with clay to remove basic nitrogen. Analysis of the feed showed the nitrogen level before

TABLE 7

REFORMING(1) OF TOSCO HYDROCRACKER 350-420°F CUT

| <u>Species Type</u> | Mole Percent(2) | | Mole Percent |
|----------------------|-----------------|-----------------|-----------------|
| | <u>Feed</u> | <u>in MB-15</u> | <u>in MB-16</u> |
| Paraffin | 24.4 | 29.6 | 29.3 |
| Cycloparaffin | 22.1 | 24.3 | 24.3 |
| Dicycloparaffin | 17.3 | 17.5 | 16.2 |
| Tricycloparaffin | 3.17 | 3.01 | 3.62 |
| Alkyl Benzene | 21.6 | 17.4 | 17.7 |
| Benzocycloparaffin | 8.15 | 5.29 | 5.14 |
| Benzodicycloparaffin | 1.96 | 1.67 | 2.08 |
| 2 Ring Aromatics | 1.19 | 1.17 | 1.53 |
| 3 Ring Aromatics | 0.09 | 0.05 | 0.07 |

(1) Reaction Conditions: MB-15: 99 LHSV, 840°F, 10.7 atm H₂.
 MB-16: 96 LHSV, 1020°F, 10.6 atm H₂.

(2) Values are \pm 5% relative.

treatment to be 2.1 wppm and after treatment it was 0.8 wppm. This did not result in any enhanced activity. The feed was then switched from the Tosco 350-420 °F cut to a CITGO 420-450 °F cut. No change in reforming effectiveness was observed. It was evident that some change in operating conditions would have to be found in order to keep the catalyst active.

Fuel Runs Under Hydrogen

The catalysts used in refinery reformers are robust enough to withstand the temperature regime in which we were operating. The units are operated at liquid space velocities of only 1-3 hr⁻¹ but they can be run for months without catalyst renewal. What is used in refinery units that was missing from our test unit was added hydrogen. It is normal practice to cycle two to three moles of hydrogen per mole of hydrocarbon through the unit during its operation. We decided to mimic this procedure for this test catalyst by increasing the operating pressure to 25 atm with added hydrogen. This proved effective in maintaining catalyst activity for our one to two hour runs.

Tables 8 through 16 detail the reforming of the eight refinery feeds under these modified conditions. Several general trends are evident. In all cases there is little change in the mole fraction of paraffin species. The cycloparaffin content decreases significantly in the lowest boiling cuts of both Tosco and CITGO feeds, there being a 17 to 25 percent decrease for the former and a 30 to 39 percent decrease for the latter. The higher conversions occurring at the higher temperatures. What is surprising is that the dicycloparaffins, the decalin analogs, appear more active than the cycloparaffins. For the Tosco feed the conversion of dicycloparaffins ranges from 33 to 41 mole percent and for the CITGO feed it ranges from 44 to 63 percent. It is to be remembered that in our model compound work the cycloparaffin methylcyclohexane was more effectively reformed than the dicycloparaffin decalin.

TABLE 8

REFORMING(1) OF TOSCO HYDROCRACKER 350-420°F CUT

| <u>Species Type</u> | Mole Percent(2) <u>Feed</u> | Mole Percent <u>in MB-19</u> | Mole Percent <u>in MB-20</u> |
|----------------------|--------------------------------|---------------------------------|---------------------------------|
| Paraffin | 24.4 | 27.7 | 24.8 |
| Cycloparaffin | 22.1 | 18.3 | 16.6 |
| Dicycloparaffin | 17.3 | 11.7 | 10.3 |
| Tricycloparaffin | 3.17 | 3.48 | 4.00 |
| Alkyl Benzene | 21.6 | 25.4 | 28.9 |
| Benzocycloparaffin | 8.15 | 8.72 | 9.04 |
| Benzodicycloparaffin | 1.96 | 2.46 | 3.34 |
| 2 Ring Aromatics | 1.19 | 2.23 | 2.95 |
| 3 Ring Aromatics | 0.09 | 0 | 0.05 |

(1) Reaction Conditions: MB-19: 141 LHSV, 840°F, 25.3 atm H₂.
 MB-20: 137 LHSV, 1020°F, 26.3 atm H₂.

(2) Values are \pm 5% relative.

TABLE 9

REFORMING(1) OF TOSCO HYDROCRACKER 420-450°F CUT

| <u>Species Type</u> | Mole Percent(2) | | |
|----------------------|-----------------|-----------------|-----------------|
| | <u>Feed</u> | <u>in MB-25</u> | <u>in MB-26</u> |
| Paraffin | 26.7 | 26.1 | 22.5 |
| Cycloparaffin | 18.0 | 13.7 | 14.4 |
| Dicycloparaffin | 14.3 | 7.60 | 7.90 |
| Tricycloparaffin | 4.98 | 5.19 | 5.26 |
| Alkyl Benzene | 20.9 | 27.5 | 28.8 |
| Benzocycloparaffin | 9.86 | 9.82 | 9.09 |
| Benzodicycloparaffin | 2.76 | 4.13 | 4.85 |
| 2 Ring Aromatics | 2.16 | 5.43 | 6.86 |
| 3 Ring Aromatics | 0.31 | 0.44 | 0.42 |

(1) Reaction Conditions: MB-25: 105 LHSV, 840°F, 25.0 atm H₂.
 MB-26: 105 LHSV, 1020°F, 25.0 atm H₂.

(2) Values are $\pm 5\%$ relative.

Table 10

REFORMING(1) OF TOSCO HYDROCRACKER 450+°F CUT

| <u>Species Type</u> | Mole Percent(2) | Mole Percent | Mole Percent |
|----------------------|-----------------|-----------------|-----------------|
| | <u>Feed</u> | <u>in MB-29</u> | <u>in MB-30</u> |
| Paraffin | 40.8 | 39.1 | 43.4 |
| Cycloparaffin | 19.4 | 16.9 | 17.4 |
| Dicycloparaffin | 10.6 | 7.28 | 4.82 |
| Tricycloparaffin | 3.83 | 4.16 | 1.66 |
| Alkyl Benzene | 11.9 | 17.1 | 18.7 |
| Benzocycloparaffin | 6.72 | 6.36 | 5.94 |
| Benzodicycloparaffin | 2.35 | 2.92 | 2.88 |
| 2 Ring Aromatics | 4.04 | 5.32 | 4.86 |
| 3 Ring Aromatics | 0.37 | 0.72 | 0.23 |

(1) Reaction Conditions: MB-29: 106 LHSV, 840°F, 25.1 atm H₂.
 MB-30: 103 LHSV, 1020°F, 25.0 atm H₂.

(2) Values are \pm 5% relative.

TABLE 11

REFORMING(1) OF TOSCO HYDROCRACKER WHOLE CUT

| <u>Species Type</u> | Mole Percent(2) | | Mole Percent |
|----------------------|-----------------|-----------------|-----------------|
| | <u>Feed</u> | <u>in MB-33</u> | <u>in MB-34</u> |
| Paraffin | 24.6 | 29.1 | 26.2 |
| Cycloparaffin | 23.3 | 16.5 | 17.7 |
| Dicycloparaffin | 18.6 | 9.78 | 9.87 |
| Tricycloparaffin | 2.84 | 4.04 | 4.04 |
| Alkyl Benzene | 21.9 | 25.9 | 25.6 |
| Benzocycloparaffin | 6.34 | 8.64 | 7.54 |
| Benzodicycloparaffin | 1.71 | 1.54 | 3.58 |
| 2 Ring Aromatics | 0.70 | 4.11 | 5.01 |
| 3 Ring Aromatics | 0 | 0.36 | 0.40 |

(1) Reaction Conditions: MB-33: 104 LHSV, 840°F, 24.6 atm H₂.
 MB-34: 102 LHSV, 1020°F, 25.6 atm H₂.

(2) Values are \pm 5% relative.

TABLE 12

REFORMING(1) OF CITGO HYDROCRACKER 350-420°F CUT

| <u>Species Type</u> | Mole Percent(2) <u>Feed</u> | Mole Percent <u>in MB-27</u> | Mole Percent <u>in MB-28</u> |
|----------------------|--------------------------------|---------------------------------|---------------------------------|
| Paraffin | 27.2 | 25.3 | 21.6 |
| Cycloparaffin | 22.3 | 15.7 | 13.7 |
| Dicycloparaffin | 15.3 | 8.53 | 5.71 |
| Tricycloparaffin | 1.15 | 1.41 | 1.58 |
| Alkyl Benzene | 22.8 | 32.9 | 38.1 |
| Benzocycloparaffin | 8.17 | 9.73 | 10.1 |
| Benzodicycloparaffin | 2.08 | 3.18 | 4.39 |
| 2 Ring Aromatics | 0.92 | 3.24 | 4.86 |
| 3 Ring Aromatics | 0 | 0 | 0 |

(1) Reaction Conditions: MB-27: 105 LHSV, 840°F, 25.0 atm H₂.
 MB-28: 105 LHSV, 1020°F, 25.0 atm H₂.

(2) Values are \pm 5% relative.

TABLE 13

REFORMING(1) OF CITGO HYDROCRACKER 420-450°F CUT

| <u>Species Type</u> | Mole Percent(2) | Mole Percent | Mole Percent |
|----------------------|-----------------|-----------------|-----------------|
| | <u>Feed</u> | <u>in MB-21</u> | <u>in MB-22</u> |
| Paraffin | 29.9 | 28.6 | 26.2 |
| Cycloparaffin | 18.9 | 15.1 | 15.1 |
| Dicycloparaffin | 12.0 | 7.05 | 6.11 |
| Tricycloparaffin | 1.60 | 2.01 | 2.35 |
| Alkyl Benzene | 20.4 | 27.3 | 29.7 |
| Benzocycloparaffin | 12.00 | 10.40 | 9.46 |
| Benzodicycloparaffin | 3.07 | 4.14 | 4.90 |
| 2 Ring Aromatics | 2.08 | 5.22 | 6.07 |
| 3 Ring Aromatics | 0 | 0.07 | 0.10 |

(1) Reaction Conditions: MB-21: 112 LHSV, 840°F, 24.5 atm H₂.
 MB-22: 114 LHSV, 1020°F, 24.6 atm H₂.

(2) Values are $\pm 5\%$ relative.

TABLE 14

REFORMING(1) OF CITGO HYDROCRACKER 450°F CUT

| <u>Species Type</u> | Mole Percent(2) | Mole Percent | Mole Percent |
|----------------------|-----------------|-----------------|-----------------|
| | <u>Feed</u> | <u>in MB-31</u> | <u>in MB-32</u> |
| Paraffin | 36.8 | 43.8 | 36.8 |
| Cycloparaffin | 21.2 | 17.5 | 21.2 |
| Dicycloparaffin | 7.13 | 4.86 | 7.12 |
| Tricycloparaffin | 1.80 | 1.67 | 1.80 |
| Alkyl Benzene | 18.4 | 18.8 | 18.4 |
| Benzocycloparaffin | 4.84 | 5.98 | 5.84 |
| Benzodicycloparaffin | 3.23 | 2.90 | 3.23 |
| 2 Ring Aromatics | 5.33 | 4.11 | 5.38 |
| 3 Ring Aromatics | 0.24 | 0.23 | 0.24 |

(1) Reaction Conditions: MB-31: 103 LHSV, 840°F, 25.0 atm H₂.
 MB-32: 102 LHSV, 1020°F, 24.6 atm H₂.

(2) Values are $\pm 5\%$ relative.

TABLE 15

REFORMING(1) OF CITGO HYDROCRACKER WHOLE FEED

| <u>Species Type</u> | Mole Percent(2) | Mole Percent | Mole Percent |
|----------------------|-----------------|-----------------|-----------------|
| | <u>Feed</u> | <u>in MB-35</u> | <u>in MB-36</u> |
| Paraffin | 32.1 | 31.2 | 26.5 |
| Cycloparaffin | 23.0 | 15.9 | 15.9 |
| Dicycloparaffin | 11.40 | 5.98 | 4.77 |
| Tricycloparaffin | 1.25 | 1.41 | 1.56 |
| Alkyl Benzene | 18.2 | 29.2 | 36.8 |
| Benzocycloparaffin | 7.29 | 8.55 | 7.48 |
| Benzodicycloparaffin | 1.95 | 3.11 | 3.50 |
| 2 Ring Aromatics | 1.66 | 4.56 | 3.52 |
| 3 Ring Aromatics | 0.07 | 0.09 | 0.02 |

(1) Reaction Conditions: MB-35: 101 LHSV, 84 °F, 24.6 atm H₂.
 MB-36: 101 LHSV, 1020 °F, 24.6 atm H₂.

(2) Values are \pm 5% relative.

TABLE 16

REFORMING(1) OF TOSCO HYDROCRACKER 350-420°F CUT

| <u>Species Type</u> | Mole Percent(2) | | |
|----------------------|-----------------|-----------------|-----------------|
| | <u>Feed</u> | <u>in MB-23</u> | <u>in MB-24</u> |
| Paraffin | 24.4 | 24.7 | 24.7 |
| Cycloparaffin | 22.1 | 20.4 | 22.5 |
| Dicycloparaffin | 17.3 | 18.1 | 18.1 |
| Tricycloparaffin | 3.17 | 3.02 | 2.94 |
| Alkyl Benzene | 21.6 | 22.1 | 21.9 |
| Benzocycloparaffin | 8.15 | 6.23 | 6.06 |
| Benzodicycloparaffin | 1.96 | 1.79 | 1.98 |
| 2 Ring Aromatics | 1.19 | 3.52 | 1.64 |
| 3 Ring Aromatics | | 0.10 | 0.08 |

(1) Reaction Conditions: MB-23: 111 LHSV, 840°F, 5.3 atm H₂.
 MB-24: 113 LHSV, 1020°F, 3.5 atm H₂.

(2) Values are $\pm 5\%$ relative.

These decreases in cycloparaffin species are accompanied by increases in the mole fractions of alkyl benzenes, benzocycloparaffins, benzodicycloparaffins, and 2 ring aromatics. Our mass spectral analyses detect some 3 ring aromatics but this level is usually too low to be considered very reliable.

The higher boiling cuts of these two refinery samples also show significant reforming activity. But again it is the dicycloparaffinic species which appear more active. Comparing the relative changes of dicycloparaffins to those of cycloparaffins in Tables 9 and 13, the 420-450 OF cuts of these feeds, it can be seen that the dicycloparaffins are almost twice as active as the cycloparaffins. Note that this is not just a case of the dicycloparaffins cracking since the paraffin content is generally unchanged. It could however be that the dicycloparaffins undergo ring opening to generate cycloparaffins which then in turn reform to aromatics. Generally one sees an increase in total aromaticity roughly equal to the decrease in naphthene content but the fraction that is due to increases in 2 ring aromatics, benzocycloparaffins, and benzodicycloparaffins does correspond well with the larger changes seen in dicycloparaffin content. Such an observation argues for ring opening being a major reaction pathway for the dicycloparaffins.

The 450+ boiling cuts of the two feeds are waxier than their lower boiling fractions. Smaller total changes of relative naphthene to aromatic content are evidenced. The whole fuels themselves show moderate reforming activity with about a 50% reduction of the dicycloparaffins and about a 25% reduction in cycloparaffins.

It can be stated then that the activity of these streams towards high space velocity catalytic reforming is reasonably good. Relative increases in total aromaticity on the order of 40% can be observed which holds promise for improvement with further changes in conditions and catalysts.

VI. Additional Reformer Runs

Considerable time was spent in finding conditions which gave reforming activity for these refinery streams. As the program developed it became clear that the third sample from Washington state would not arrive in time to allow adequate feed preparation and testing. A program modification was authorized to investigate what factors might be responsible for the complete lack of activity at lower pressures without added hydrogen. It had been thought that the generation of hydrogen by reforming of these naphthene rich streams would be sufficient protection to permit operation of the test unit for the short time need to make our runs. It must be emphasized again that this study is not a catalyst screening program and that the catalyst supplied by UOP, Inc. is being used under conditions for which it has not been optimized.

Several material balances were performed to test factors which might be detrimental to catalyst activity. Table 17 lists mass spectral analyses of two runs made at 300 LHSV, the originally proposed operating condition, with the Tosco 350-420°F cut as feedstock and with a guard bed of catalyst upstream from the reactor. It was thought that maybe the clay treatment used for feed pretreatment in material balance MB 17 (see Appendix C) was not sufficiently selective for catalyst poisons. If the lack of activity was due some trace impurity then a guard bed should allow operation for some small period of time. No reforming activity is in evidence from the mass spectral analyses of feed and product.

A sample of catalyst was obtained from another manufacturer and tested at 100 LHSV under hydrogen and at 300 LHSV without added hydrogen. The result was similar to that found for the UOP catalyst, i.e., moderate activity in the former case and no activity in the latter. This catalyst did give higher conversions than the UOP catalyst but it must be mentioned that the UOP catalyst is an old formulation which has undoubtedly been improved and generated newer formulations under different labels since the earlier USAF/Shell work. These results are in Table 18.

TABLE 17

REFORMING(1) OF TOSCO HYDROCRACKER 350-420°F CUT

| <u>Species Type</u> | Mole Percent(2) | Mole Percent | Mole Percent |
|----------------------|-----------------|-----------------|-----------------|
| | <u>Feed</u> | <u>in MB-37</u> | <u>in MB-38</u> |
| Paraffin | 24.4 | 24.6 | 24.8 |
| Cycloparaffin | 22.1 | 20.9 | 22.7 |
| Dicycloparaffin | 17.3 | 15.0 | 18.3 |
| Tricycloparaffin | 3.17 | 3.36 | 3.01 |
| Alkyl Benzene | 21.6 | 23.8 | 21.5 |
| Benzocycloparaffin | 8.15 | 6.96 | 6.05 |
| Benzodicycloparaffin | 1.96 | 2.67 | 2.20 |
| 2 Ring Aromatics | 1.19 | 2.55 | 0.06 |
| 3 Ring Aromatics | 0.10 | 0.08 | 0.06 |

(1) Reaction Conditions: MB-37: 316 LHSV, 840°F, 10 atm H₂.
 MB-38: 304 LHSV, 1020°F, 10 atm H₂.

(2) Values are $\pm 5\%$ relative.

TABLE 18
REFORMING⁽¹⁾ OF TOSCO HYDROCRACKER 350-420°F CUT

| <u>Species Type</u> | Mole Percent ⁽²⁾ <u>Feed</u> | Mole Percent <u>in MB-38</u> | Mole Percent <u>in MB-40</u> |
|----------------------|--|---------------------------------|---------------------------------|
| Paraffin | 24.4 | 19.2 | 21.8 |
| Cycloparaffin | 22.1 | 12.9 | 20.1 |
| Dicycloparaffin | 17.3 | 7.50 | 14.9 |
| Tricycloparaffin | 3.17 | 3.36 | 3.01 |
| Alkyl Benzene | 21.6 | 34.5 | 22.4 |
| Benzocycloparaffin | 8.15 | 12.2 | 7.27 |
| Benzodicycloparaffin | 1.96 | 5.50 | 3.12 |
| 2 Ring Aromatics | 1.19 | 4.33 | 1.57 |
| 3 Ring Aromatics | 0.10 | 0 | 0.12 |

(1) Reaction Conditions: MB-39: 101 LHSV, 840°F, 24.6 atm H₂.
 MB-40: 316 LHSV, 840°F, 11 atm H₂.
 Both runs used an Engelhard catalyst.

(2) Values are $\pm 5\%$ relative.

An attempt was made to remove chloride from the catalyst by washing it with ammonium hydroxide and rinsing it with water. This did remove chloride from the catalyst but the treated catalyst showed no enhanced activity for reforming. Mass spectral data for material balances MB23 and MB24 in Appendix C show the results of these tests.

The final two runs of the program were made using 50/50 v/v mixtures of Tosco 350-420°F cut and methylcyclohexane. It was thought that perhaps the enrichment of the feed stream with the very active methylcyclohexane would afford enough initial hydrogen overpressure to maintain catalyst activity. This proved not to be the case as no reforming was evident. These results are tabulated in Appendix C.

VII. CONCLUSIONS

There are several conclusions to be drawn from the results of this program

- 1) The current domestic supply of naphthene rich turbine fuel material is quite large. Approximately 500,000 barrels per day of this material is being produced.
- 2) The potential of this resource for endothermic fuel applications shows promise since the supply is generally sulfur free.
- 3) These materials can be reformed at high space velocity e.g., 100 LHSV. Conversions demonstrated in this preliminary study are on the order of 25-30 % of the naphthene content. This was accompanied by cracking side reactions.

APPENDIX B

MATERIAL BALANCE DATA

Forty-two experimental runs were performed during the course of this project. They encompassed tests to determine the behaviors of: 1) model compounds such as methylcyclohexane and decalin; 2) turbine fuel cuts and whole turbine fuels generated from refinery hydrocracker effluents; and 3) process and catalyst sensitivity to various reaction conditions and catalyst pretreatment. The data and calculated closures for all these runs, with the exception of run number 2 which was aborted, are detailed in the tables that follow.

TABLE B-1
MATERIAL BALANCE DATA FOR MB01

FEED: Methylcyclohexane

| | |
|--|----------|
| Reactor Temperature : | 1050°F |
| Reactor Pressure : | 35.8 atm |
| LHSV : | 107 |
| Grams Feed Input : | 3300 |
| Grams Liquid Product: | 3061 |
| Grams Gaseous Product: (Avg. MW = 2.0) | NA* |
| Grams Coke : | NA |
| Mass Balance Closure: | 85% |

* NA = Not Analyzed

NO MATERIAL BALANCE WAS CALCULATED FOR MB02

TABLE B-3
MATERIAL BALANCE DATA FOR MB03

FEED: Methylcyclohexane

| | |
|------------------------|---------------------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 8.6 atm |
| LHSV : | 96.2 |
| Grams Feed Input : | 1490 |
| Grams Liquid Product: | 1370 |
| Grams Gaseous Product: | 83.6 |
| (Avg. MW = 3.0) | |
| Grams Coke : | 0.30 ⁽¹⁾ |
| Mass Balance Closure: | 97.5 |

TABLE B-4
MATERIAL BALANCE DATA FOR MB04

FEED: Methylcyclohexane

| | |
|--|---------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 7.3 atm |
| LHSV : | 96.5 |
| Grams Feed Input : | 1420 |
| Grams Liquid Product: | 1246 |
| Grams Gaseous Product: (Avg. MW = 3.0) | 93.9 |
| Grams Coke : | 0.30 |
| Mass Balance Closure: | 94.4 |

TABLE B-5
MATERIAL BALANCE DATA FOR MB05

FEED: Decalin

| | |
|---|--------------------|
| Reactor Temperature : | 840 ^o F |
| Reactor Pressure : | 10.3 atm |
| LHSV : | 90.6 |
| Grams Feed Input : | 1585 |
| Grams Liquid Product: | 1587 |
| Grams Gaseous Product: (Avg. MW = --) | 0 |
| Grams Coke : | 0.44 |
| Mass Balance Closure: | 100.2 |

TABLE B-6
MATERIAL BALANCE DATA FOR MB06

FEED: Decalin

| | |
|------------------------|---------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 9.7 atm |
| LHSV : | 90.3 |
| Grams Feed Input : | 1580 |
| Grams Liquid Product: | 1582 |
| Grams Gaseous Product: | 0 |
| (Avg. MW = --) | |
| Grams Coke : | 0.44 |
| Mass Balance Closure: | 100.2 |

TABLE B-7
MATERIAL BALANCE DATA FOR MB07

FEED: Decalin

| | |
|--|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 10.3 atm |
| LHSV : | 88.0 |
| Grams Feed Input : | 1540 |
| Grams Liquid Product: | 1524 |
| Grams Gaseous Product: (Avg. MW = 2.0) | 50.4 |
| Grams Coke : | 0.15 |
| Mass Balance Closure: | 102.2 |

TABLE B-8
MATERIAL BALANCE DATA FOR MB08

FEED: Decalin

| | |
|------------------------|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 10.3 atm |
| LHSV : | 92.0 |
| Grams Feed Input : | 1610 |
| Grams Liquid Product: | 1589 |
| Grams Gaseous Product: | NA |
| (Avg. MW = ---) | |
| Grams Coke : | 0.15 |
| Mass Balance Closure: | 98.7 |

NA=not analyzed

TABLE B-9
MATERIAL BALANCE DATA FOR MB09

FEED: Decalin

| | |
|--|---------------------|
| Reactor Temperature : | 1020 ^o F |
| Reactor Pressure : | 10.3 atm |
| LHSV : | 990.8 |
| Grams Feed Input : | 2600 |
| Grams Liquid Product: | 2573 |
| Grams Gaseous Product: (Avg. MW = 2.0) | 19.2 |
| Grams Coke : | 0.06 |
| Mass Balance Closure: | 99.7 |

TABLE B-10
MATERIAL BALANCE DATA FOR MB10

FEED: Decalin

| | |
|--|---------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 9.9 atm |
| LHSV : | 1011 |
| Grams Feed Input : | 1990 |
| Grams Liquid Product: | 2105 |
| Grams Gaseous Product: (Avg. MW = 2.0) | 14.2 |
| Grams Coke : | 0.6 |
| Mass Balance Closure: | 106.5 |

TABLE B-11
MATERIAL BALANCE DATA FOR MB11

FEED: Methylcyclohexane

| | |
|------------------------|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 10.3 atm |
| LHSV : | 968 |
| Grams Feed Input : | 2250 |
| Grams Liquid Product: | 2224 |
| Grams Gaseous Product: | 27.7 |
| (Avg. MW = 2.02) | |
| Grams Coke : | 0.03 |
| Mass Balance Closure: | 100.1 |

TABLE B-12
MATERIAL BALANCE DATA FOR MB12

FEED: Methylcyclohexane

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 10.3 atm |
| LHSV : | 994 |
| Grams Feed Input : | 2310 |
| Grams Liquid Product: | 2282 |
| Grams Gaseous Product: (Avg. MW = 2.0) | 48.5 |
| Grams Coke : | 0.03 |
| Mass Balance Closure: | 100.1 |

TABLE B-13
MATERIAL BALANCE DATA FOR MB13

FEED: Tosco 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 10.0 atm |
| LHSV : | 287 |
| Grams Feed Input : | 4780 |
| Grams Liquid Product: | 4867 |
| Grams Gaseous Product: (Avg. MW = 6.06) | 4.80 |
| Grams Coke : | 0.70 |
| Balance Closure: | 101.9% |

TABLE B-14
MATERIAL BALANCE DATA FOR MB14

FEED: Tosco 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 10.3 atm |
| LHSV : | 299 |
| Grams Feed Input : | 4980 |
| Grams Liquid Product: | 4957 |
| Grams Gaseous Product: (Avg. MW = 25.2) | 31.69 |
| Grams Coke : | 0.70 |
| Mass Balance Closure: | 100.2% |

TABLE B-15
MATERIAL BALANCE DATA FOR MB15

FEED: Tosco 350-420°F Cut

| | |
|---|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 10.7 atm |
| LHSV : | 98.8 |
| Grams Feed Input : | 1645 |
| Grams Liquid Product: | 1600 |
| Grams Gaseous Product: (Avg. MW = 22) | 32 |
| Grams Coke : | 0.83 |
| Mass Balance Closure: | 98.7 |

TABLE B-16
MATERIAL BALANCE DATA FOR MB16

FEED: Tosco 350-420°F Cut

| | |
|---|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 10.6 atm |
| LHSV : | 96.1 |
| Grams Feed Input : | 800 |
| Grams Liquid Product: | 786 |
| Grams Gaseous Product: (Avg. MW = 30) | 78 |
| Grams Coke : | 0.83 |
| Mass Balance Closure: | 102.4 |

TABLE B-17
MATERIAL BALANCE DATA FOR MB17

FEED: Tosco 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 10.6 atm |
| LHSV : | 93 |
| Grams Feed Input : | 1550 |
| Grams Liquid Product: | 1556 |
| Grams Gaseous Product: (Avg. MW = 4.86) | 7.3 |
| Grams Coke : | 2.00 |
| Mass Balance Closure: | 100.1 |

TABLE B-18
MATERIAL BALANCE DATA FOR MB18

FEED: Citgo 420-450°F Cut

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 10.5 atm |
| LHSV : | 94.5 |
| Grams Feed Input : | 1580 |
| Grams Liquid Product: | 1620 |
| Grams Gaseous Product: (Avg. MW = 4.73) | 7.1 |
| Grams Coke : | 1.66 |
| Mass Balance Closure: | 103.1 |

TABLE B-19
MATERIAL BALANCE DATA FOR MB19

FEED: Tosco 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 25.3 atm |
| LHSV : | 141 |
| Grams Feed Input : | 2344 |
| Grams Liquid Product: | 2305 |
| Grams Gaseous Product: (Avg. MW = 2.11) | 6.12 |
| Grams Coke : | 0.28 |
| Mass Balance Closure: | 98.6 |

TABLE B-20
MATERIAL BALANCE DATA FOR MB20

FEED: Tosco 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 26.3 atm |
| LHSV : | 137 |
| Grams Feed Input : | 1696 |
| Grams Liquid Product: | 1620 |
| Grams Gaseous Product: (Avg. MW = 2.97) | 11.58 |
| Grams Coke : | 0.28 |
| Mass Balance Closure: | 96.2% |

TABLE B-21
MATERIAL BALANCE DATA FOR MB21

FEED: Citgo 420-450°F Cut

| | |
|--|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 24.5 atm |
| LHSV : | 112 |
| Grams Feed Input : | 940 |
| Grams Liquid Product: | 922 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 14.7 |
| Grams Coke : | 0.38 |
| Mass Balance Closure: | 99.7% |

TABLE B-22
MATERIAL BALANCE DATA FOR MB22

FEED: Citgo 420-450°F Cut

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 24.6 atm |
| LHSV : | 114 |
| Grams Feed Input : | 950 |
| Grams Liquid Product: | 929 |
| Grams Gaseous Product: (Avg. MW = 4.69) | 19.7 |
| Grams Coke : | 0.38 |
| Mass Balance Closure: | 99.9% |

TABLE B-23
MATERIAL BALANCE DATA FOR MB23

FEED: Tosco 350-420°F Cut

| | |
|------------------------|---------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 5.3 atm |
| LHSV : | 111 |
| Grams Feed Input : | 925 |
| Grams Liquid Product: | 926 |
| Grams Gaseous Product: | 0 |
| (Avg. MW = ---) | |
| Grams Coke : | 0.45 |
| Mass Balance Closure: | 100.1% |

TABLE B-24
MATERIAL BALANCE DATA FOR MB24

FEED: Tosco 350-420°F Cut

| | |
|--|---------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 3.5 atm |
| LHSV : | 113 |
| Grams Feed Input : | 940 |
| Grams Liquid Product: | 925 |
| Grams Gaseous Product: (Avg. MW =----) | 0 |
| Grams Coke : | 0.45 |
| Mass Balance Closure: | 98.5% |

TABLE B-25
MATERIAL BALANCE DATA FOR MB25

FEED: Tosco 420-450°F Cut

| | |
|--|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 25.0 atm |
| LHSV : | 105 |
| Grams Feed Input : | 880 |
| Grams Liquid Product: | 870 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 7.68 |
| Grams Coke : | 0.31 |
| Mass Balance Closure: | 99.8% |

TABLE B-26
MATERIAL BALANCE DATA FOR MB26

FEED: Tosco 420-450°F Cut

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 25.0 atm |
| LHSV : | 105 |
| Grams Feed Input : | 880 |
| Grams Liquid Product: | 867 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 6.67 |
| Grams Coke : | 0.31 |
| Mass Balance Closure: | 99.3% |

TABLE B-27
MATERIAL BALANCE DATA FOR MB27

FEED: Citgo 350-420°F Cut

| | |
|------------------------|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 25.0 atm |
| LHSV : | 105 |
| Grams Feed Input : | 865 |
| Grams Liquid Product: | 858 |
| Grams Gaseous Product: | 8.9 |
| (Avg. MW = 2.02) | |
| Grams Coke : | 0.20 |
| Mass Balance Closure: | 100.2% |

TABLE B-28
MATERIAL BALANCE DATA FOR MB28

FEED: Citgo 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 25.0 atm |
| LHSV : | 105 |
| Grams Feed Input : | 870 |
| Grams Liquid Product: | 864 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 11.1 |
| Grams Coke : | 0.20 |
| Mass Balance Closure: | 100.6% |

TABLE B-29
MATERIAL BALANCE DATA FOR MB29

FEED: Tosco 450+^oF Cut

| | |
|--|--------------------|
| Reactor Temperature : | 840 ^o F |
| Reactor Pressure : | 25.1 atm |
| LHSV : | 106 |
| Grams Feed Input : | 880 |
| Grams Liquid Product: | 865 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 11.9 |
| Grams Coke : | 0.51 |
| Mass Balance Closure: | 99.7% |

TABLE B-30
MATERIAL BALANCE DATA FOR MB30

FEED: Tosco 450+°F Cut

| | |
|---|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 25.0 atm |
| LHSV : | 103 |
| Grams Feed Input : | 860 |
| Grams Liquid Product: | 847 |
| Grams Gaseous Product: (Avg. $MW = 2.02$) | 12.7 |
| Grams Coke : | 0.51 |
| Mass Balance Closure: | 100.0% |

TABLE B-31
MATERIAL BALANCE DATA FOR MB31

FEED: Citgo 450+^oF Cut

| | |
|--|--------------------|
| Reactor Temperature : | 840 ^o F |
| Reactor Pressure : | 24.6 atm |
| LHSV : | 103 |
| Grams Feed Input : | 850 |
| Grams Liquid Product: | 842 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 11.7 |
| Grams Coke : | 0.78 |
| Mass Balance Closure: | 100.5% |

TABLE B-32
MATERIAL BALANCE DATA FOR MB32

FEED: Citgo 450+°F Cut

| | |
|------------------------|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 24.5 atm |
| LHSV : | 102 |
| Grams Feed Input : | 840 |
| Grams Liquid Product: | 813 |
| Grams Gaseous Product: | 11.9 |
| (Avg. MW = 2.02) | |
| Grams Coke : | 0.78 |
| Mass Balance Closure: | 98.3% |

TABLE B-33
MATERIAL BALANCE DATA FOR MB33

FEED: Tosco Whole Fuel

| | |
|--|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 24.6 atm |
| LHSV : | 104 |
| Grams Feed Input : | 860 |
| Grams Liquid Product: | 870 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 8.9 |
| Grams Coke : | 0.58 |
| Mass Balance Closure: | 102.0% |

TABLE B-34
MATERIAL BALANCE DATA FOR MB34

FEED: Tosco Whole Fuel

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 24.6 atm |
| LHSV : | 102 |
| Grams Feed Input : | 850 |
| Grams Liquid Product: | 828 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 9.2 |
| Grams Coke : | 0.58 |
| Mass Balance Closure: | 98.6% |

TABLE B-35
MATERIAL BALANCE DATA FOR MB35

FEED: Citgo Whole Fuel

| | |
|--|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 24.6 atm |
| LHSV : | 101 |
| Grams Feed Input : | 830 |
| Grams Liquid Product: | 826 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 8.7 |
| Grams Coke : | 0.35 |
| Mass Balance Closure: | 100.6% |

TABLE B-36
MATERIAL BALANCE DATA FOR MB36

FEED: Citgo Whole Fuel

| | |
|------------------------|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 24.6 atm |
| LHSV : | 101 |
| Grams Feed Input : | 830 |
| Grams Liquid Product: | 810 |
| Grams Gaseous Product: | 13.1 |
| (Avg. MW = 2.02) | |
| Grams Coke : | 0.35 |
| Mass Balance Closure: | 99.2% |

TABLE B-37
MATERIAL BALANCE DATA FOR MB37

FEED: Tosco 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 10.0 atm |
| LHSV : | 316 |
| Grams Feed Input : | 2630 |
| Grams Liquid Product: | 2512 |
| Grams Gaseous Product: (Avg. MW = 2.08) | 9.15 |
| Grams Coke : | 1.24 |
| Mass Balance Closure: | 95.9% |

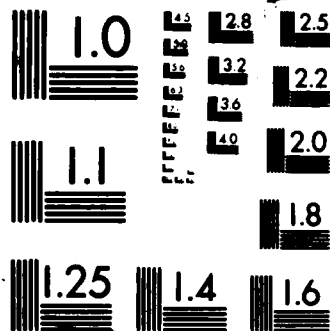
EVALUATION OF NAPHTHENE RICH TURBINE FUELS AS HEAT
SINKS FOR HYPERSONIC AIRCRAFT(U) J AND A ASSOCIATES INC
GOLDEN CO B J LILLIS JAN 87 AFWL-RR-87-2026
F33615-86-C-2664 F/G 21/4

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PHOTOCOPY RESOLUTION TEST CHART

TABLE B-38
MATERIAL BALANCE DATA FOR MB38

FEED: Tosco 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 10.0 atm |
| LHSV : | 304 |
| Grams Feed Input : | 2530 |
| Grams Liquid Product: | 2550 |
| Grams Gaseous Product: (Avg. MW = 2.82) | 0.85 |
| Grams Coke : | 1.24 |
| Mass Balance Closure: | 100.9% |

TABLE B-39
MATERIAL BALANCE DATA FOR MB39

FEED: Tosco 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 24.6 atm |
| LHSV : | 101 |
| Grams Feed Input : | 840 |
| Grams Liquid Product: | 825 |
| Grams Gaseous Product: (Avg. MW =2.20) | 8.69 |
| Grams Coke : | 1.07 |
| Mass Balance Closure: | 99.4% |

This material balance used a catalyst different from those of all other runs except MB40.

TABLE B-40
MATERIAL BALANCE DATA FOR MB40

FEED: Tosco 350-420°F Cut

| | |
|--|--------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 11.0tm |
| LHSV : | 316 |
| Grams Feed Input : | 2630 |
| Grams Liquid Product: | 2592 |
| Grams Gaseous Product: (Avg. MW = 3.1) | 5.6 |
| Grams Coke : | 1.07 |
| Mass Balance Closure: | 98.8% |

This material balance used a catalyst different from that used in all other runs except MB39.

TABLE B-41
MATERIAL BALANCE DATA FOR MB41

FEED: 50/50 v/v Methylcyclohexane + Tosco 350-420°F Cut

| | |
|------------------------|----------|
| Reactor Temperature : | 840°F |
| Reactor Pressure : | 10.8 atm |
| LHSV : | 289 |
| Grams Feed Input : | 1160 |
| Grams Liquid Product: | 1170 |
| Grams Gaseous Product: | 0 |
| (Avg. MW = ---) | |
| Grams Coke : | NA |
| Mass Balance Closure: | 100.9% |

TABLE B-42
MATERIAL BALANCE DATA FOR MB42

FEED: 50/50 v/v Methylcyclohexane + Tosco 350-420°F Cut

| | |
|--|----------|
| Reactor Temperature : | 1020°F |
| Reactor Pressure : | 24.6 atm |
| LHSV : | 103 |
| Grams Feed Input : | 1660 |
| Grams Liquid Product: | 1660 |
| Grams Gaseous Product: (Avg. MW = 2.02) | 33.7 |
| Grams Coke : | 0.44 |
| Mass Balance Closure: | 102.1% |

APPENDIX D
TBP DISTILLATIONS

TABLE D-1

THP DISTILLATION REPORT

| | | | | | | | | |
|--------------------|--|-----------------|-----------|------------------|--------------------|----------------|-------------------|---------------------|
| Dist Type | Batch Still | Dist # | 101 + 102 | Analyst | C. M. Smits | | | |
| J&A Number | 56609 | Proj # | 3429 | Date | 10-28-86 - 11-5-86 | | | |
| Sample Description | Tosco Refinery Hydrocracker Diesel Cut | | | | | | | |
| Cut Number | Temp. Range F at 1 Atm. | Weight (gms) | Wt % | Specific Gravity | °API 60/60 | Volume (ml) | Volume Percent | % Volume Percent |
| 56609-A | IBP(346)-420 | 62,711 | 37.13 | 0.8326 | 38.5 | 75,319 | 37.23 | 37.23 |
| 56609-B | 420-450 | 34,935 | 20.69 | 0.8411 | 36.7 | 41,535 | 20.53 | 57.76 |
| | Total Distilled | 97,646 | 57.82 | | | 116,854 | 57.76 | |
| 56609-C | 450+ | 71,105 | 42.10 | 0.8344 | 38.1 | 85,217 | 42.12 | 99.88 |
| | Totals | 168,751 | | | | 202,071 | | |

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Actual Balance Data:

| | | | | | | | | |
|-----------------|---------|------|---------|-------|----------------|--------|-------|-------|
| Charge: | 168,890 | gms. | 202,312 | mls. | Charge Data: | = | 53.4 | gal. |
| Recovery: | 168,751 | gms. | 202,071 | mls. | SG = | 0.8348 | API = | 38.0° |
| Loss + Hold-Up: | 139 | gms. | 241 | mls. | Residuum Data: | = | 22.5 | gal. |
| % Recovery: | 99.92 | Wt % | 99.88 | Vol % | SG = | 0.8344 | API = | 38.1° |

Disk: Form

Doc: JAAOC14

10/15/86

TBP DISTILLATION REPORT

| | | | | | |
|----------------------|---------|------|---------|----------------------|-------------------------|
| Actual Balance Data: | | | | | |
| Charge: | 169.930 | gms. | 206.878 | mils. Charge Data: | = 54.7 gal. |
| Recovery: | 170.130 | gms. | 207.060 | mils. | SG = 0.8214 API = 40.8° |
| Loss + Hold-Up: | (200) | gms. | (182) | mils. Residuum Data: | = 16.0 gal. |
| % Recovery: | 100.12 | Wt % | 100.09 | Vol % | SG = 0.8218 API = 40.7° |

Disk: Form
Doc: JAA0014
10/15/86

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